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Biobased, thermoreversibly crosslinked polyesters

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Biobased, thermoreversibly crosslinked polyesters

A styrene-free alternative to currently employed resins

Martijn Beljaars

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A styrene-free alternative to currently employed resins

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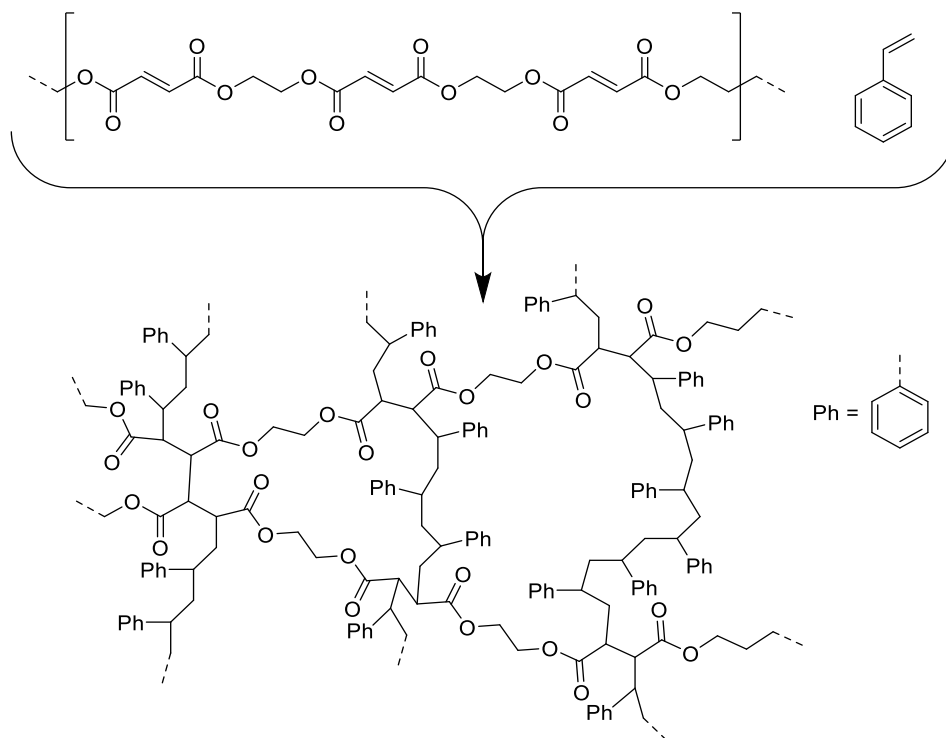
Chapter 1

Introduction

1.1 : Introduction

Crosslinked resins are usually employed in highly demanding applications where very specific properties are required of the resulting material: i.e. excellent chemical resistance, mechanical strength and dimensional stability¹. Unsaturated polyester (UP) resins neatly fit all these high demands; they possess the required mechanical properties due to the fact that they consist of polyester chains that are covalently crosslinked, essentially, the resulting material consists of one large network. Therefore, any significant deformation of this highly crosslinked material requires the breaking of chemical bonds. A testament to the success of UP resins is the volume at which they are produced: worldwide, an estimated 2.2 billion kg of UP resin are produced annually². Besides the superior (mechanical) properties of the final product, UP resins possess other qualities that render them highly desirable: the uncrosslinked material is stable and can be stored for a long time; the curing time can be adjusted by adding different amounts of curing agent and, finally, the uncrosslinked resin is a liquid, which makes it particularly well suited for embedding materials like fibers that can lend extra strength or reduce density. UP resins are liquids because they consist of (relatively short) unsaturated polyester chains that are dissolved in styrene (Scheme 1). The exact compositions of these resins depend on the application and producer, but on average they contain between 35 to 60 wt% of styrene, which acts as a reactive solvent. Indeed, styrene dissolves the polyester chains and, by a free radical polymerization mechanism, it then polymerizes *in situ*, thus resulting in the crosslinking of the final material (Scheme 1). Crosslinking is performed by addition of an initiator, usually methyl ethyl ketone peroxide is being used as radical initiator, combined with cobalt octoate as accelerator. The exact crosslinking mechanism is complex as it involves styrene homopolymerization, polyester homopolymerization utilizing the double bonds present in the unsaturated polyester and graft copolymerization of both³. The mechanism is further complicated by changes in the physical structure during the curing process: most importantly gelation and vitrification (i.e. the transition from amorphous liquid to a glass). Nevertheless, the resulting material is highly crosslinked.

Scheme 1: Representation of crosslinking in a styrene based UP resin



Unfortunately, despite its many merits, there are serious disadvantages to the use of styrene in this (or any other) polymers. Firstly, styrene is a volatile organic compound which has been classified as a “*Group 2B, possibly carcinogenic to humans*” by the International Agency for Research on Cancer (IARC)⁴. The metabolite of styrene, styrene oxide has been detected in workers exposed to styrene and IARC has classified this as a “*Group 2A, probable human carcinogen*”. The significance of this problem is illustrated by the loss percentages of styrene for various applications of UP resins (Table 1). Considering the styrene content of these resins (up to 60%, *vide supra*) it is evident that for any application other than closed processes special precautions have to be taken in order to prevent exposure to this dangerous chemical.

Process	Styrene loss (%)
Gelcoat spray	10-14
Spray-up, non-LSE resin	7-10
Gelcoat, brush	6-8
Filament winding	5-7
Hand Lay-up, non-LSE resin	4-6
Spray-up, LSE / LSC resin	4-6
Topcoat, spray	4-5
Topcoat, brush	3-4
Hand Lay-up, LSE / LSC resin	3-4
Pultrusion	1-3
Polymer concrete etc.	1-3
Continuous lamination	1-2
SMC/BMC manufacturing	1-2
SMC/BMC processing	1-2
Closed processes (RTM/RTM Light/Infusion)	<1

Table 1: Styrene loss for various processes⁵

LSE/C = Low styrene emission/content, SMC/BMC = Sheet/Bulk molding compound, RTM = Resin transfer molding

Besides the hazards of using styrene, there are other reasons to consider a replacement: the currently employed styrene is obtained from fossil fuels. Considering the prospect of declining oil reserves, a steady increase of global energy demands and environmental concerns⁶, a sustainable, bio-based alternative becomes more and more appealing. Given the availability of natural resources, the expected positive impact on carbon emissions and the scale of

styrene consumption, the potential merits of such a sustainable process are immediately evident. Fortunately, there are various options to increase the sustainability of a process in general, and a styrene based polymerization reaction in particular.

1.2 The first step: increasing sustainability or “going green”

The most straightforward way towards a sustainable process is by replacing styrene with itself, i.e. fossil based styrene with green, biobased styrene. This bio-based styrene would be identical in all aspects to the currently used one, save for its origin. The use of bio-based chemicals reduces the dependence on fossil fuels and, more importantly, their sustainable manufacturing will reduce the accompanying carbon emissions. Due to the scale of annual consumption of styrene, any minor improvement in sustainability is expected to have a major global effect. The direct substitution of chemicals by their bio-based alternatives is known as *drop-in replacement*, the viability of which is mainly dependent on the availability of the chemical to be replaced. Fortunately there is a large, ever expanding, library of biobased chemicals already commercially available, and with some minor chemical modifications this library can be exponentially expanded (Figure 1)⁷.

The commercial viability of drop-in replacements is demonstrated by various examples that include, besides the most famous green ethanol⁸, also green ethylene obtained from sugar⁹, lignin derived phenolics in wood glue formulations¹⁰ and benzene, toluene and xylene (BTX) obtained from wood chips¹¹. Using a drop-in replacement for styrene would be a step in the right direction towards increasing the green carbon content of UP resins. However, in order to obtain a fully biobased material all other involved chemicals (e.g. propylene glycol and maleic anhydride / maleic acid) used to make the polyester should be substituted as well. Unfortunately, despite the vast library of drop-in replacements, a green substitution is not always immediately available. In these cases an alternative solution may be found in the use of a comparable alternative chemical. Such a compound should have similar chemical and physical properties (e.g. reactivity and solubility) to make it a suitable substitute. Recent successful

judging the importance of these approaches. A 2002 article describes the European waste policies by implementing a waste pyramid¹⁵ (Figure 2). In this waste pyramid the most favorable option (prevention) is listed at the top and the least favorable (disposal) at the bottom. The current best practice for UP resins consists of mechanical destruction (e.g. grinding) and subsequently using the resulting particles as filler material in new applications. This reduces the amount of virgin material needed (Material Recovery in Figure 2).

On the other hand characteristic applications of these ground resins are typically low cost and performance materials, e.g. roadside markers or asphalt bedding. This entails a significant decrease in value along the overall chain starting from highly valuable UP resins. This is even more evident when considering the fate of any other discarded UP resins not re-used in this manner: i.e. incineration (Energy Recovery) or dumping in landfills (Final Disposal).

Moving up one tier in the pyramid (i.e. to the Reuse option) exposes an intrinsic problem of UP resins and thermosets in general. As mentioned, the covalent bonds that form the crosslinks provide many beneficial mechanical properties, however they also severely limit any possibility for repairing or reclaiming spent material. During curing, a covalent network is formed; this network is so inert that it is factually impossible to reverse the curing reaction in order to obtain the starting materials once more. Moreover due to the inertness of the network, any damage sustained by the material (microfractures or cracking) cannot be repaired in a feasible way. This often means that in order to repair minor damages an entire piece has to be replaced. The inability for minor repairs combined with the rigidity of these resins renders them completely unsuitable for reuse in the same (or similarly valued) application (*cradle-to-cradle*¹⁶). To enable the reuse of these kinds of material, different crosslinking chemistry has to be considered altogether. If the bonds that make the network can be made in a reversible way, i.e. they can be broken and reformed on command by some external stimulus (e.g. temperature¹⁷, light, pH etc.), then a recyclable system should be obtained¹⁸. After opening the crosslinks, the starting materials would be (re)obtained, ready to be re-cured and used in a new application, or the same application without any concessions to mechanical properties. Furthermore, if the crosslinks can be broken by mild conditions (temperature rather than mechanical force); any embedded components could be reclaimed and potentially reused as well. Finally,

the implementation of reversible crosslinks should result in a material that can easily be repaired. Any broken crosslinks can be reformed under the same conditions as when the material was initially created. This potential for self-repair is known as *self-healing*, a concept closely related to the one of (thermo)reversible networks¹⁹.

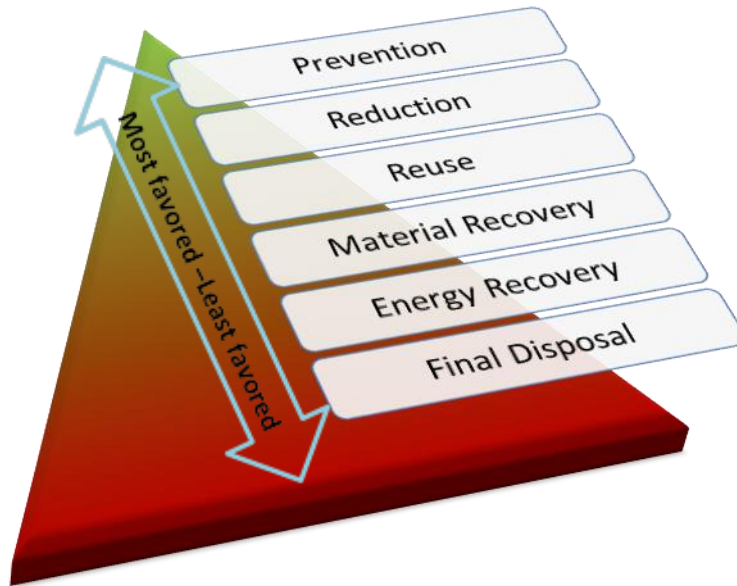


Figure 2: The hierarchy of waste management, listing the most favored solution at the top.

1.4 Enabling recyclability: Self-healing materials

Traditionally, there are several methods for repairing a damaged polymer resin: welding, patching or *in situ* curing. Not all methods are applicable to each material however. Welding enables the closing of cracks through rejoining the fractured surfaces or fusing new material to the damaged region. During the welding process, the material undergoes a number of transitions: surface rearrangement, surface approach, wetting and diffusion^{20,21}. It relies on chain entanglements between the contacting surfaces and it may be aided by the use of solvents and increased temperature²². Due to the requirement of chain entanglement, welding is mostly used in thermoplastic materials, as the chain ends in most thermosets

are usually not of sufficient length to enable entanglements. Furthermore, the entangled region will possess significantly different mechanical properties with respect to the crosslinked regions. Patching constitutes covering or replacing the damaged area with new material, either through mechanical fastening or through the use of adhesives. The success of patching is dependent on factors such as the interface between the patch and original material²³, the presence and orientation of reinforcing fibres^{24,25}, and the thickness of the patch^{26,27}. Due to the fact that extra material is added to patch the damage, this method is not always suited for a given application. The final method: *in situ* curing involves the application of new, uncured starting material, which will diffuse into the damaged region, increasing the contact area. The starting material can be used as an adhesive for any possible patches that are applied to the region as well²⁸. Most of these methods require the use of extra material and the properties obtained are usually inferior to those of the starting material. Self-healing eliminates the need for additional material while resulting in principle in no loss of mechanical properties. Self-healing has been achieved in two fundamentally different ways: extrinsic and intrinsic self-healing. Extrinsic self-healing is achieved via incorporation of capsules containing (low molecular weight) additives that can act as healing agents upon cracking, thus effectively performing *in situ* curing without the need of additional material²⁹⁻³⁴. Intrinsic self-healing involves the modification of the polymer to enable the healing of cracks in response to an external stimulus like heat^{17,35-37} or light³⁸⁻⁴¹. Ideally, in the near future a crack should be repairable merely by applying heat. As stated, in order to enable cradle-to-cradle recycling of these thermosets, as well as potential reclamation of embedded materials and possibly enabling self-healing, reversible crosslinking is the first requirement.

1.5 Thermally Reversible Networks: supramolecular crosslinking

There are various reversible crosslinking methods: hydrogen bonding, electrostatic interactions and (covalent) adaptive networks. Hydrogen bonding and electrostatic interactions can be classified as supramolecular bonds. When mechanical stress is applied to the material the weaker supramolecular bonds will fail first and, due to their reversible nature, these can later be reformed.

Hydrogen bonding is a non-covalent interaction between a hydrogen atom and a different one which is more electronegative. With a strength of 5-30 kJ/mol, a hydrogen bond is stronger than a van der Waals interaction, yet weaker than a covalent bond. Hydrogen bonds have been employed as crosslinking device in polymers for the first time by Klok et al⁴². However for this particular system, at increased temperatures (over 70 °C) the zero-shear viscosities increased sharply with temperature, indicating that most likely side reactions occurred. The hydrogen bonds are expected to break at elevated temperatures, leading to a lower viscosity.

The relatively weak bond strength is easily addressed by simply increasing the number of hydrogen bonds per crosslink as demonstrated by Chino and Ashiura⁴³ who described a rubber system crosslinked by using triazole rings. By using 3-amino 1,2,4-triazole, solidification of the normally liquid rubber was observed at room temperature. The mechanical properties of the resulting material are comparable to those of Sulphur vulcanized rubbers. There are some drawbacks to this method: the synthesis required is quite complex and has only been performed on lab-scale. More importantly, however: the obtained glass transition temperature of -60 °C is by far too low to be a competitor for styrene UP-resins and there is no mention of the effect of water on bond stability. Generally speaking, the presence of water has a devastating effect on hydrogen bonds. All this makes this particular system unsuitable for replacing styrene UP resins.

Another widely investigated method of reversible crosslinking is the use of ionomers^{44,45}. These materials are defined by the presence of ionic groups along the polymer backbone, or on pendant groups which can be present in many different forms e.g. sulfonate⁴⁶, carboxylic acid⁴⁷ or ammonium salt⁴⁸ groups. The counter-ion used is just as versatile; and is the main source of variability in material properties^{49,50} and mechanical behavior⁵¹⁻⁶³ of ionomers. These materials have generated a lot of scientific and industrial interest due to their many applications like fuel cells⁶⁴⁻⁶⁷, membranes^{65,68} and exfoliating aids during processing⁶⁹. Of particular interest for this work is the application of ionic bonds in thermoreversible crosslinking. The ionic crosslink is an electrostatic interaction that occurs by clustering of the ionic groups. These groups tend to associate in multiplets, which in turn organize themselves into clusters (Figure 3). The morphology of these clusters has been extensively studied and is shown to

have an established^{49,50} effect on the properties of the resulting material such as thermal and mechanical behaviour⁵¹.

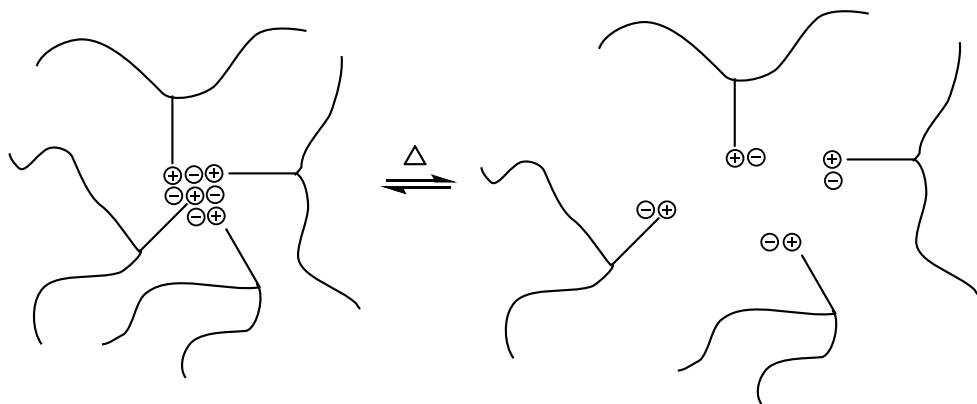


Figure 3: Association and dissociation of ionic groups in an ionomer

For example, the crystallization rate for sulfonated syndiotactic polystyrene was found⁷⁰ to be inversely proportional to the ionic radius of the counter-ion. Other factors that influence the mechanical properties of these materials are the position of the ionomeric group along the chain, and its distance from the polymer backbone⁷¹ as well as the type of ionomeric group employed (e.g. ionomers bearing sulfonic groups are reported to display higher tensile strength than those bearing carboxylic groups⁷²). Unfortunately, though the properties of these materials can be influenced by the type of counter-ion, the fact remains that a metal is needed in all of the systems described. From an environmental and sustainable point of view this makes these materials less appealing. Furthermore, for most applications of ionomers (especially membranes, and in particular those used in fuel cells) water uptake is considered a crucial factor, since it influences the stability of the membrane⁷³. When considering an alternative for UP-resins, water uptake is disastrous for most of the applications. This also renders ionomeric materials unsuitable candidates for replacing styrene UP resins.

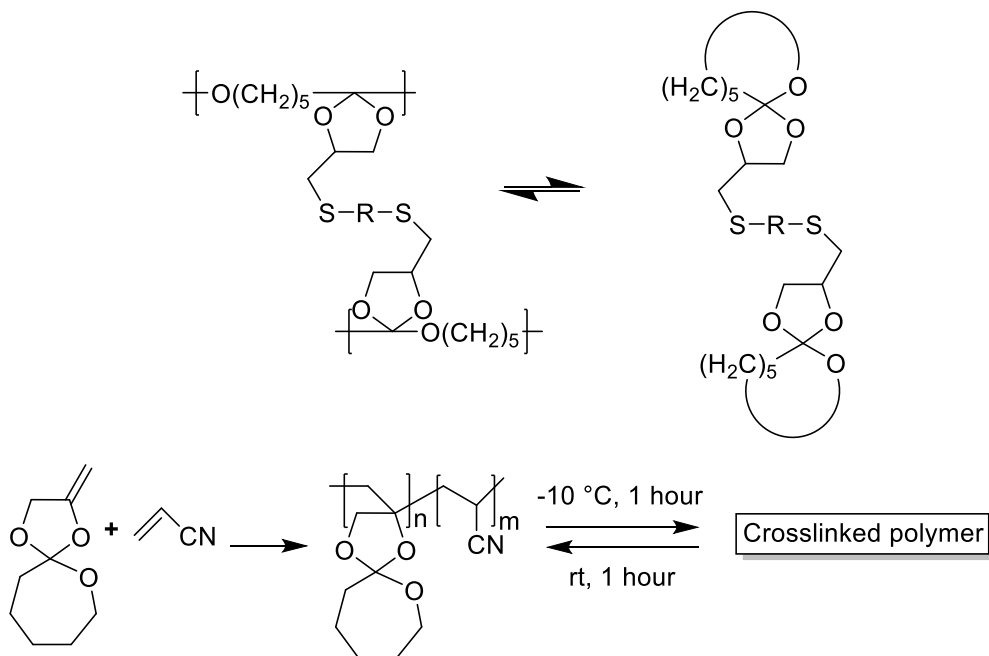
There is an intrinsic problem when considering supramolecular crosslinking methods: by definition, in order to achieve self-healing, the crosslinking bonds have to be weaker than the bonds in the polymer matrix. In this way, when force is applied to the material the weaker bonds will fail first, which can later be reformed. Seeing as toughness is one of the main appeals of UP-resins, a proper

replacement should preferably be based on covalent crosslinking. Covalently crosslinked materials in general possess better creep resistance, high modulus, high fraction strength and excellent solvent resistance. Some options in this respect are discussed in the following.

1.6 Thermally Reversible Networks: covalent crosslinking

There are various thermoreversible systems known involving covalent bonds, for instance ester bond rupture which employs a dithiol as crosslinker. The system described by Endo *et al* in the original publication⁷⁴ can be better described as a reversible polymerization reaction (Scheme 2, top). A later publication describes⁷⁵ a system where the technique is employed as a true reversible crosslinker: an acrylonitrile matrix is reversibly crosslinked by pendant spiro orthoester groups (Scheme 2, bottom).

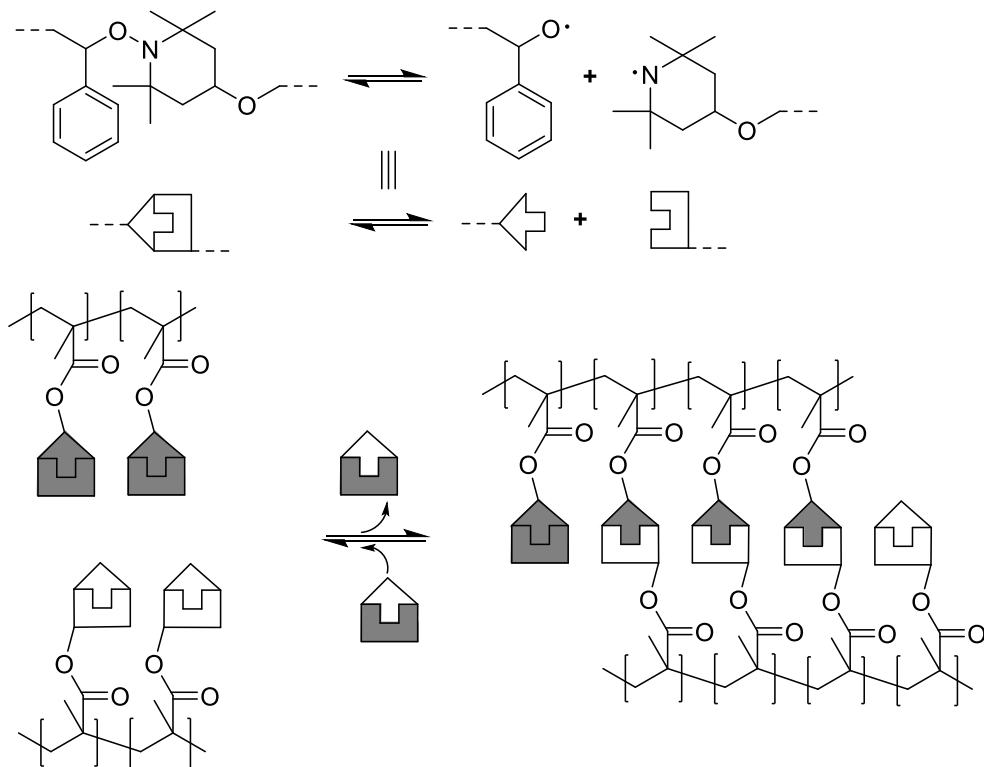
Scheme 2: ester amide bond rupture (top), employed as reversible crosslinker (bottom).



Unfortunately, this method cannot be applied to polyesters as these will depolymerize as well under the de-crosslinking reaction conditions.

Another possible method of reversible covalent crosslinking is the use of a radical exchange reaction. Higaki *et al* described⁷⁶ a polymer containing a pendant alkoxamine group based on 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO). This alkoxamine is able to undergo reversible C-O bond cleavage yielding two radicals (Scheme 3). These radicals can reconnect to yield the original alkoxamine unit. Inter- and intramolecular C-C coupling is not observed due to fast capping of the formed carbon radical by a nitroxide radical. Unfortunately, the decoupling temperature of 100 °C is somewhat low for the considered application as UP-resin substitute. Furthermore, the need to add or remove an external compound in order to obtain the desired configuration (e.g. adding extra alkoxamine in order to obtain the decrosslinked material, and removing the alkoxamine to obtain the crosslinked material) severely limits the potential applications of this method.

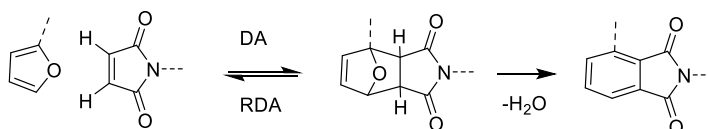
Scheme 3: reversible crosslinking via radical exchange reaction. Top: schematic representation of the radical pair, bottom: the coupling and decoupling reaction influenced by the addition or removal of alkoxamine.



Finally, in the field of adaptive covalent networks, the most commonly employed reaction is the 2+4 cycloaddition reported by, and named after, Diels and Alder⁷⁷. It is a thermoreversible 2+4 cycloaddition which can be performed by various combinations of functional groups e.g. furan and maleimide, anthracene and maleimide, cyclopentadiene and fulvene. This variance in possible pairs ultimately results in precise control over the properties of the resulting material: The Diels-Alder (DA) addition reaction is in fact an equilibrium that at lower (application) temperatures favors the adduct, yet above a certain temperature shifts towards the dissociated compounds. The association and dissociation temperatures are dependent on the specific groups utilized (Table 2). From these options, the furan-maleimide pair stands out: its crosslinking temperature is sufficiently low to allow for the formation of a network by using a relatively low amount of energy.

Furthermore, the decrosslinking temperature is sufficiently high as to not hamper its use in most applications, yet not so high as to risk decomposition of the polymer matrix during decrosslinking. Finally, various furanics can also be obtained from sugars, making them an interesting candidate from a sustainability point of view. The furan-maleimide reaction has been widely and extensively studied⁹⁶⁻⁹⁸ and the first reported polymer based on this pair was already reported in 1986^{99,100}. However, while this research did employ the Diels-Alder reaction to make linear polymers of difuranes and dimaleimides, the authors then proceeded to aromatize the product in order to obtain the desired polymer, preventing any retro-Diels-Alder reactions taking place (Scheme 4).

Scheme 4: Diels-Alder equilibrium and aromatization



The first mention of a thermoreversible linear polymer was in 1994 when Kuramoto *et al* described¹⁰¹ an A-A B-B type polymer obtained by combining a difuran and bismaleimide. It then took until 2002 when Chen *et al* reported^{102,103} the first thermoreversibly crosslinked system by combining a tetra-furan with bis- and tris-maleimides. All the systems described so far are polymers obtained from coupling furanic and maleimide-containing monomers. A different strategy involves the implementation of the Diels-alder reaction only as a crosslinking tool between existing polymers. In order to achieve this, a polymer containing furane or maleimide groups in the backbone or as pendant groups needs to be synthesized. In 1979 Stevens *et al* reported¹⁰⁴ the crosslinking reaction of styrene containing pendant maleimide groups. The reversibility was not discussed until 1992, when the reversible gelation of the system was finally reported¹⁰⁵. Since then many systems have been described that incorporate the Diels-Alder reaction as crosslinking tool^{37,106}. Judging by the variance of polymer matrices employed, it seems that Diels-Alder crosslinking is a perfect fit for replacing styrene based UP-resins.

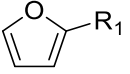
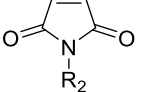
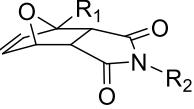
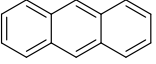
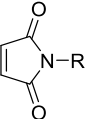
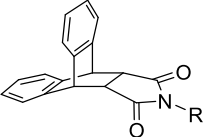


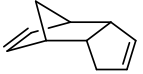
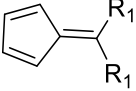
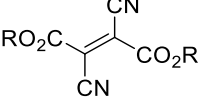
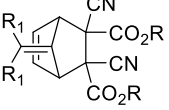
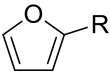

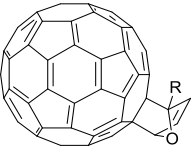

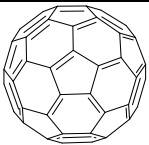
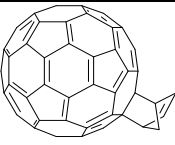
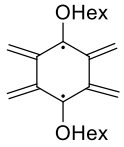

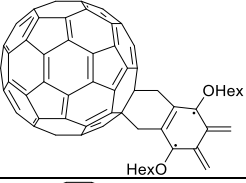
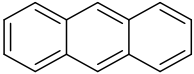

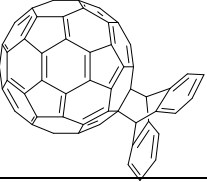

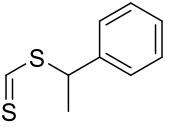
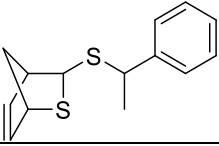
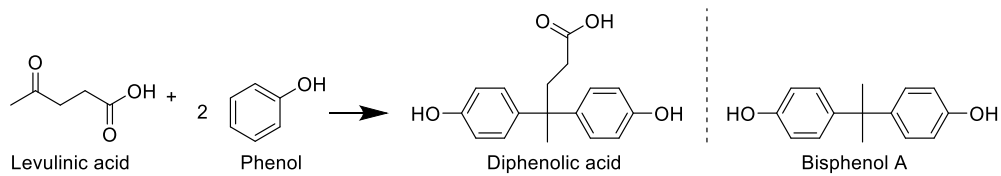
Diene	Dienophile	Adduct	T _{DA}	T _{RDA}	Ref
			50-80	110-170	78-81
			125	250	82-84
			25-120	150-215	85-87
			RT	50-100	86,88,89
			RT	180	90
			RT	95	91
			214	n.a.	92
			RT	60-82	93
			RT	80-95	94,95

Table 2: Coupling (T_{DA}) and decoupling (T_{RDA}) temperatures of various Diels-Alder couples

1.7 Monomer selection

Having established the merits of reversible crosslinking, and determined that the current systems are unsuited for such an approach, the use of a different monomer should be considered. Considering all of the above, there are three requirements that can be formulated for this monomer: it must be able to be incorporated in a polyester, it must be obtainable via a sustainable route and finally, it must possess a furanic or maleimide functionality, or sufficient extra functionality to incorporate one. The first, most obvious candidate is furandicarboxylic acid (FDCA). Although this monomer is readily incorporated in a polyester matrix¹⁰⁷ and obtainable in sustainable fashion¹⁰⁸, proof-of-principle experiments have demonstrated that the methoxyester of FDCA is not active in the (DA) reaction with maleimide. The next option would be employing a furanediol. However, recently a polyester was reported¹⁰⁹ including the furanediol which is able to undergo reversible (DA) crosslinking. The material obtained is too flexible to fulfill most of the requirements defined for UP-resins. An excellent candidate is levulinic acid, which is produced commercially from cellulose in a large scale (10000 megaton in 2017 up to 50000 megaton in 2019 from a single plant)¹¹⁰ and is relatively easily converted into diphenolic acid by condensation with phenol (Scheme 5). Diphenolic acid possesses a diol functionality, making it suitable to be incorporated in a polyester. Furthermore, it possesses an additional pendant acid group that can be converted to accommodate a DA moiety. Furfurylamine seems an excellent candidate for this as it contains an amine group, which can be converted into an amide, which in turn reduces the risk of any transesterification occurring in the final polyester, and it is a bio-based chemical typically obtained from furfural. Due to its structural similarity to bisphenol A (see Scheme 5), which allegedly possesses estrogenic properties, diphenolic acid has been placed on a watch list for expected toxicity. However, as the research described herein entails a proof-of-principle study this concern has been preliminarily discarded in order to investigate the potential possibilities before optimizing the system before implementation.

Scheme 5: Levulinic acid and its conversion to diphenolic acid, a structural analogue to bisphenol A



1.8 Contents of this thesis

The aim of this work was to devise a “human friendly” alternative to currently employed unsaturated polyester resins. In order to be able to compete, the resulting material should have the mechanical properties commonly ascribed to thermoset materials. At the same time the material should aim for maximum sustainability, using as many bio-based chemicals as possible. Already realizing at the early stages of the research that sustainability should not only come from the resources employed, but also the application and disposal of the material, the goal of this research was: the development of a biobased polymer able to undergo reversible crosslinking in order to enable recycling of the material at end of life.

Chapter 2 describes the search for a proper monomer: one that is both biobased and suitable for polymerization and functionalization. After settling on diphenolic acid, its modification, incorporation into a polymer and testing of the resulting material are discussed.

Chapter 3 describes the further modification of the polymer obtained in chapter 2. This modification is carried out in order to enable milder processing conditions. This chapter describes the modification, the effects on the processing conditions and the resulting material.

After obtaining the desired polymer with the processing conditions outlined in chapter 3, the properties of the resulting crosslinked product were improved by blending with a rubber. This was necessary in order to overcome the brittle nature of the prepared polymer. Chapter 4 describes the resulting change in properties upon incorporation of the functionalized rubber in the UP resin matrix.

In order to better understand the crosslinked material on a chemical level and to find the possible ways of tuning its mechanical properties, a range of different crosslinkers has been investigated. The effect of the type of crosslinker as well as the amount has been investigated, and the results are presented in chapter 5.

The final chapter attempts to complete the value chain by providing a technological assessment of the initial reaction: the formation of diphenolic acid as well as the final stage of the material: implementation. An attempt is made to improve upon the former by employing a different process. While the latter is

emulated by tests performed on samples reinforced with fibrous materials. In keeping with the sustainability mindset natural fibers are employed.

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Chapter 2

Bio-based aromatic polyesters reversibly crosslinked via Diels- Alder reaction

2.1 Abstract

Diphenolic acid is functionalized with furfuryl amine and subsequently incorporated in a (partly) bio-based polyester through interfacial polycondensation with terephthalic chloride. The furan groups present in the resulting polyester are able to form a thermoreversible covalent network with different bismaleimide moieties via the Diels-Alder (DA) reaction. Analysis of the polymer network by $^1\text{H-NMR}$ clearly shows formation of both stereoisomers (endo and exo) possible from Diels-Alder coordination of furan and maleimide. Furthermore, it was found that these isomers can be reversibly interchanged at temperatures below the reported retro Diels-Alder reaction temperature, a phenomenon often claimed, yet up to date never directly observed, for thermally reversible polymeric systems. Finally, a proof-of-principle for reversibility and recyclability is shown.

Keywords: bio-based, short-chain, polyester, furan, bismaleimide, thermoreversibility, Diels-Alder, endo-exo regeoisomers, recyclability.

2.2 Introduction

The uncertain prices of crude oil, the increasing awareness of carbon emissions as well as the resulting desire to become gradually independent of fossil fuels constitute strong driving forces behind the search for sustainable alternatives to fossil-fuel based chemicals¹. An ever-increasing number of processes are “going green”. The first, and most obvious approach towards this end is the direct substitution of petrol-based chemicals by their bio-based counterparts. There are various examples of commercially available chemicals, obtained from renewable resources, like polyethylene² and succinic acid³. These *drop-in* products require no special adaptation before using them as they are essentially the same chemical, merely isolated from a different feedstock. The transition towards the use of green chemicals is not always smooth since obtaining these chemicals is hindered by a few complicating factors. Most predominantly, it is often cumbersome to obtain them in high purities as bio based chemicals are often obtained from a mixture of usually very similar and hard to separate chemicals⁴. This problem is particularly pressing for green monomers as these require very high purities in order to be able to undergo successful polymerization reactions⁵. Fortunately,

there are cases where a mixture of products has successfully been used as green component. Indeed, up to 75% of phenol used in wood adhesives can be replaced by a mixture of various phenolic compounds obtained from lignin⁶ and polyols from vegetable oils have successfully been employed as crosslinker in polyurethanes⁷. However, these are rare exceptions rather than common practice. Nevertheless, despite these complications, several successful implementations of green chemicals as monomers have been reported⁸⁻¹⁰, reducing both the carbon footprint of the associated materials and their fossil-fuel dependency. Unfortunately, despite these positive aspects, simple substitution of oil-based chemicals with biomass-derived ones does not provide an exhaustive answer to the sustainability issue as waste-streams (i.e. the waste produced at the end of the product life) remain virtually unaffected. Green thermoplastic materials might be recyclable in a “cradle-to-cradle” fashion as this is generally true for polymeric materials with physical (e.g. van der Waals) interactions between the chains¹¹. However, thermoset materials are notoriously and factually impossible to recycle according to a “cradle-to-cradle” approach¹². This is obviously true independently of their origin, i.e. whether oil- or bio-based. In the past decade many efforts have been made in order to increase the recyclability of these materials, and a promising recent advancement is the use of thermoreversible crosslinking by means of the Diels-alder reaction⁸⁻¹⁰. The reversible nature of the Diels Alder reaction has been successfully applied in self-healing polymers¹³⁻²¹. Most popular is the reaction between a furan and maleimide^{12,22} mainly due to fast kinetics and wide availability of the reacting groups¹², although systems based on cyanofumarate and vulvene²³ or anthracene and maleimide²⁴ have also been reported. The application of the Diels-Alder reaction in crosslinking has many advantages: as the formed bonds are covalent, the superior properties attributed to thermosets will be retained (e.g. due to their crosslinked structure, these usually possess superior barrier and mechanical properties as well as higher chemical resistance than most thermoplastic ones). Furthermore as the reaction is an equilibrium one and its extent can be easily influenced by changing temperature, it constitutes an ideal candidate for use as crosslinking reaction. Finally, the temperatures for bond formation, and the reverse reaction, which yields the de-crosslinked product, are sufficiently far apart (namely 50-80°C and 110-170°C respectively for furan and maleimide) to ensure that the obtained materials have a large application window.

The conceptual combination of thermal reversibility with the “green” character of available monomers constitutes a possible solution to the problems outlined above, thus providing in principle a lower carbon footprint as well as recyclability (*cradle-to-cradle*) of the end product. In this context, the presence of functional groups (e.g. –OH ones), often considered a major drawback of green chemicals, when compared to fossil-fuel based ones, might be conveniently exploited to provide the chemicals with an added functionality. A paradigmatic example is constituted by diphenolic acid (DPA), a structural analog to bisphenol A²⁵ obtained via a condensation reaction of levulinic acid²⁶ with phenol. The only difference with bisphenol A is the presence of an extra carboxylic acid. Bisphenol A is widely used as monomer in polycarbonate and epoxy resin synthesis, but also employed as rigidifier in polyester resins. Apart from the fact that it is currently obtained from non-renewable resources, it is also a toxic chemical with shown oestrogenic properties. Polycarbonates and polyesters have been successfully synthesized using unmodified DPA^{27,28}, or after protection of the acid group²⁹. However, the acidic group might also be employed to provide this monomer with the desired (*vide supra*) Diels-Alder active moiety.

Aim of this work is to ideally combine the two strategies towards sustainability: i.e. the bio-based character and the possibility for thermally reversible crosslinking and thus possibility for recycling. To this end, DPA was modified with furfuryl amine to obtain a furan-functionalised diol. The incorporation of this monomer into a fully aromatic novel polyester is described based on known polymerization concepts. Finally the obtained polymer was crosslinked by employing the Diels-Alder reaction with a bismaleimide in order to provide a preliminary proof of principle for the possibility to recycle the end product.

2.3 Experimental section

2.3.1 Chemicals:

4,4'-bis(hydroxyphenyl)valeric acid (Diphenolic acid, DPA) 95%, 2-methyltetrahydrofuran (MeTHF) anhydrous, N,N'-Carbonyldiimidazole (CDI) 97%, Terephthaloylchloride 99+%, 1,1(methylenedi-4,1-phenylene)bismaleimide 95% were purchased from Sigma-Aldrich and used as received. Furfurylamine 99+%

was purchased from Sigma-Aldrich and distilled prior to use. Dodecyl bismaleimide was synthesized as described in literature³⁰.

2.3.2 Equipment:

¹H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz using DMSO-*d*₆ as a solvent. ¹H-NMR spectra of samples at elevated temperature were recorded on a Varian Mercury Plus 500 MHz using DMSO-*d*₆ as a solvent. PPM values are given relative to tetramethylsilane (TMS). Thermogravimetric analysis was performed on a Mettler Toledo TGA. The samples were weighed (ca. 10 mg) and placed in the analyser. Subsequently the temperature was raised from 25 °C to 900 °C at a heating rate of 10 °C per minute under N₂ atmosphere. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer differential scanning calorimeter Pyris 1 under N₂ atmosphere. Before DSC's the sample was weighed (ca. 12 mg) and subsequently heated from 25 °C to 180 °C. Multiple cycles were performed at a heating rate of 10 °C/min throughout the measurements. DMTA measurements were performed using a Rheometrics scientific solid analyzer (RSA II) under air using dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 5 °C/min. GPC measurements were performed on a HP1100 equipped with three 300x7.5 mm PLgel 3 μm MIXED-E columns in series using a GBC LC 1240 RI detector. Average molecular weight calculations were performed with the PSS WinGPC Unity software from Polymer Standards Service. The following conditions were used: THF as eluent at a flow rate of 1 ml min⁻¹; 140 bar, a column temperature of 42 °C, 20 μl injection volume and a 10 mg ml⁻¹ sample concentration. Toluene was used as a flow marker and polystyrene samples with different molecular weights were used as calibration standard. Pressing of samples was performed in a Taunus-Ton press type VS up 150A.

2.3.3 GPC

GPC measurements were performed to determine the average chain length and while absolute values cannot be given due to the absence of a suitable reference calibration, the spectra obtained across various samples confirm a consistent distribution of chain lengths between batches.

2.3.4 Synthesis of DPA-fur

Diphenolic acid (5 g, 17.5 mmol), 2-methylhydrofuran (30 mL) and *N,N'*-carbonyldiimidazole (1.2 equivalent, 3,398 g, 21 mmol) were charged to a dry three-neck round bottomed flask connected to a cooler under N₂. The reaction was stirred under reflux conditions (90°C) for two h. Furfurylamine (1.2 equivalent, 1.85 mL, 21 mmol) was added and the reaction was stirred at 90°C for an additional 5 hours. The reaction mixture was then allowed to cool to room temperature, diluted with additional 2-methylhydrofuran (45 ml). The solution was washed with 1M HCl (2 x 37 mL), 0.1 M NaOH (2 x 47 mL) and brine (1 x 15 mL) successively. Evaporation of the organic layer yields a yellow oil. Final purification by recrystallization from ethanol gave 3.26 g (51,1%) of white solid.

¹H NMR (300 MHz, DMSO-d₆) δ 9.16 (s, 2H, OH) 8.19 (t, 1H, NH) 7.53 (s, 1H, fur-*p*) 6.93 (d, 4H, benzene-*o*) 6.62 (d, 4H, benzene-*m*) 6.35 (t, 1H, fur-*m*) 6.18 (d, 1H, fur-*o*) 4.19 (d, 2H, N-CH₂) 2.17 (t, 2H, -CH₂-) 1.86 (t, 2H, -CH₂-) 1.45 (s, 3H, -CH₃).

2.3.5 Polymerization (DPA-fur/tereph)

DPA-fur (1.755 g, 4.8 mmol), tert-butyl ammonium bromide (0.152 g, 8.7 wt.% on DPA-fur), sodium hydroxide (0.384 g, 9.6 mmol) and water (45 mL) were charged to a one-neck round bottomed flask (250mL). The mixture was stirred vigorously. Terephthaloyl chloride (0.975 g, 4.8 mmol) dissolved in chloroform (45 mL) was added to the reaction mixture. The reaction was stirred vigorously for 2 h. Precipitation in methanol (1800 mL) yielded 2.20 g (95.6%) of white solid.

¹H NMR (300 MHz, DMSO-d₆) δ 8.42-7.95 (m, 4H, aromatic not next to ester) 7.53 (s, 1H, fur-*p*) 7.42-7.12 (m, 8H, aromatic next to ester) 6.34 (s, 1H, fur-*m*) 6.19(s, 1H, fur-*o*) 4.21 (d, 2H, N-CH₂) 2,38(broad s, 2H, -CH₂-) 1.95 (broad s, 2H, -CH₂-) 1.63 (s, 3H, -CH₃).

2.3.6 DMTA sample preparation via compression molding

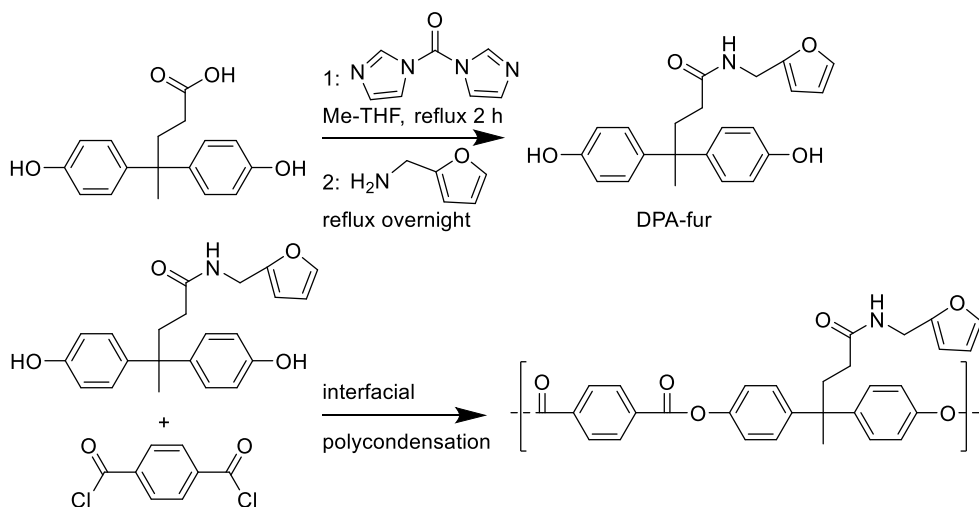
First, a mixture of polymer and bismaleimide was prepared by dissolving the desired amount of bismaleimide in a minimal amount of chloroform (e.g. 0.25 g polymer, 0.09 g of bismaleimide in 1 ml of CHCl₃). Mixing and successive solvent removal by rotary evaporation yielded a cross-linked film of polymer. This film was dried overnight in an oven at 60°C then frozen in liquid nitrogen and ground to particles using an IKA industrial hand grinder. This powder was pressed into

bars (6 mm wide, 54 mm long and 1 mm thick). Pressing was performed at 4 MPa, at a temperature of 150°C for 15 minutes. The material was expected to and did behave as a flowing thermoplastic polymer as this temperature is above the RDA decoupling temperature as well as above the T_g of the un-cross-linked polymer. The samples are cooled slowly inside the press (~30 min) to allow formation of a rigid network through DA coupling. Afterwards the samples were placed in an oven at 50 °C for 24 hours to ensure complete crosslink formation.

2.4 Results and discussion

The overall strategy for the synthesis of the desired polymers relies on the possibility of modifying DPA and functionalizing it (Scheme 1, top) with a Diels Alder reactive group (in this case furan). The employed reaction conditions, based on similar ones for amidation reactions³¹, entail the use of an intermediate (the imidazole peptide), subsequently reacted with fufurylamine to yield the desired product. This synthetic strategy allows for very controlled reaction conditions and high purity and acceptable yield of the end product. Indeed, after crystallization the DPA-fur is obtained in 51.1% yield as an off-white powder characterized by a ¹H NMR spectrum with no relevant traces of impurities (Figure 1). DPA-fur is then subsequently polymerized with terephthaloyl chloride in a two-phase system (Scheme 1, bottom) as described in the literature³².

Scheme 1: top: modification of DPA to DPA-fur, bottom: polymerization of DPA-fur with adipoyl chloride



Clean polymer formation is evident from the complete disappearance of the signals at δ 9.4 ppm in ^1H NMR (corresponding to the OH group on the DPA-fur monomer). Furthermore, aromatic protons from both terephthaloyl chloride and the DPA-fur shift significantly. Two distinct groups of peaks can be identified, one at δ 7.42-7.12 ppm belonging to the aromatic protons next to an ester bond containing 8 protons (4 *o*-from the DPA-fur, and 4 from the terephthaloyl monomer), the other group at δ 8.42-7.95 ppm contains 4 protons (the *o*-protons from DPA-fur away from the ester bond).

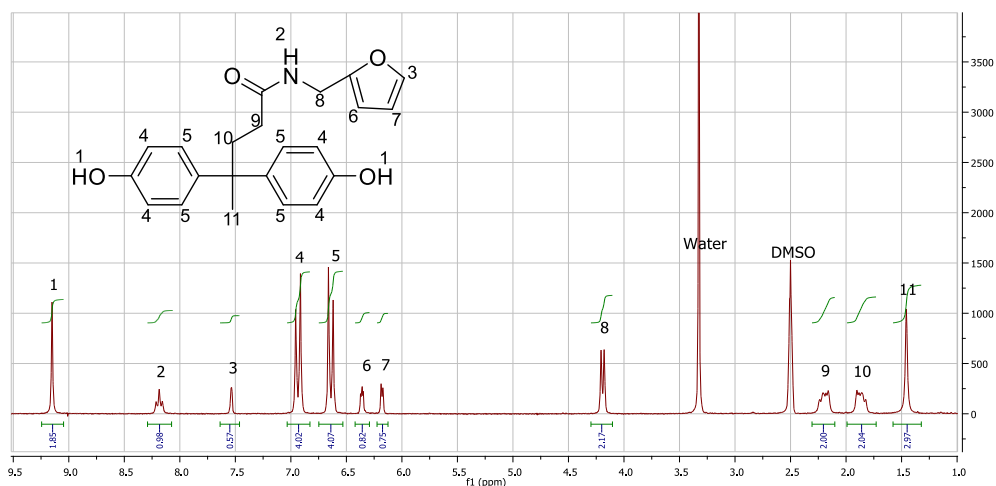
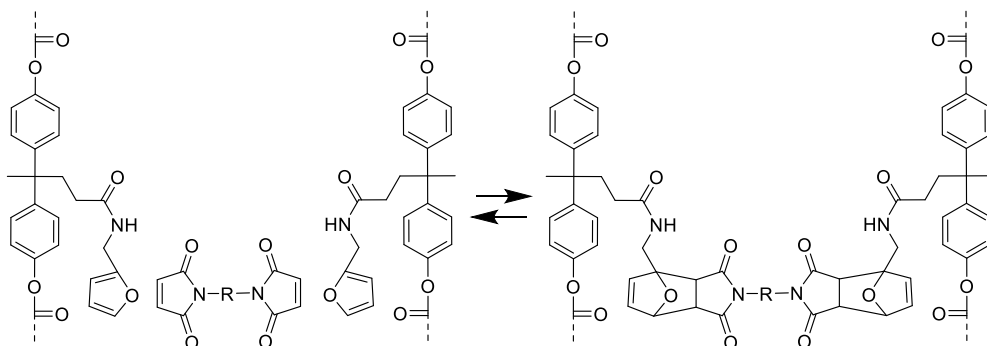


Figure 1: NMR spectrum of DPA-fur

Crosslinking of the prepared polymer via Diels Alder has been achieved by mixing it with an equimolar amount of bismaleimide in DMSO. The system is expected to crosslink by reaction of the pendant furan moieties with the maleimide groups (Scheme 2).

Scheme 2: Diels-alder crosslinking of polymer chains. R=(CH₂)₁₂, (C₆H₄)-CH₂-(C₆H₄)(see Table 1)



The reaction was initially carried out in DMSO in order to visually observe gel formation (indicative of the formation of a network structure) as well as preliminarily investigate its reversibility as a function of temperature. Two types of bismaleimide were added in various ratios and the gelation time (defined as the time it takes the stirrer to stop spinning), a rough indication for the gel formation kinetics, was determined (Table 1).

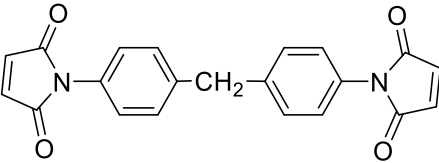
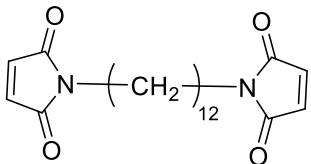
Ratio maleimides to furanes (mol:mol)	1:1	2:1	3:1	4:1
	Gelation time (min)			
 1,1'-(methylenedi-1,4-phenylene)bismaleimide	45	32	25	15
 Dodecyl bismaleimide	368	226	190	143

Table 1: Gelation times for various ratios of two different bismaleimides

In first instance it is worth noticing how both bismaleimides are able to induce gel formation, thus indicating network formation. It is also evident that the aromatic bismaleimide displays faster kinetics than the aliphatic one. The significant difference in gelation times might be related to different reaction kinetics. On the other hand this might also be due to the possibility for the aliphatic crosslinker (because of its flexible nature) of backbiting coordination where both maleimide groups attach to the same polymer chain. The aromatic bismaleimide is expected to be far too rigid to be able to coordinate in this fashion³³. Furthermore increasing the maleimide to furan ratio leads to a decrease in gelation time. This has been observed for other polymeric systems crosslinked in the same way¹² and is most probably related to the second-order kinetics (first order in the bismaleimide) of the crosslinking reaction.

In an attempt to elucidate the mechanism of crosslinking at molecular level, various NMR experiments were performed. First a sample containing uncrosslinked polymer and bismaleimide in a 1:1 ratio of maleimide to furan groups in DMSO-d₆ was prepared. Immediately after mixing an NMR spectrum was recorded (spectrum I in Figure 2). Next the sample was heated to 50°C for 3 hours; this should ensure complete formation of the crosslinks. Afterwards another NMR spectrum was recorded and the signals attributed to the DA-adduct

of furan and maleimide could clearly be detected (spectrum II in Figure 2). There have been various reports describing^{12,34} the assignments of these signals based on model compounds. Interestingly there are two clearly distinct peaks for the *endo* and *exo* adducts visible. To the best of our knowledge this is the first direct confirmation for the formation of both species since similar works on different systems describe an NMR spectrum of a crosslinked polymer network³⁴, but only see a single peak which is attributed to both isomers. When the sample is subsequently heated to 150°C for 5 minutes and a new spectrum is recorded the adduct signals disappear indicating the RDA reaction has completely occurred (spectrum III in Figure 2).

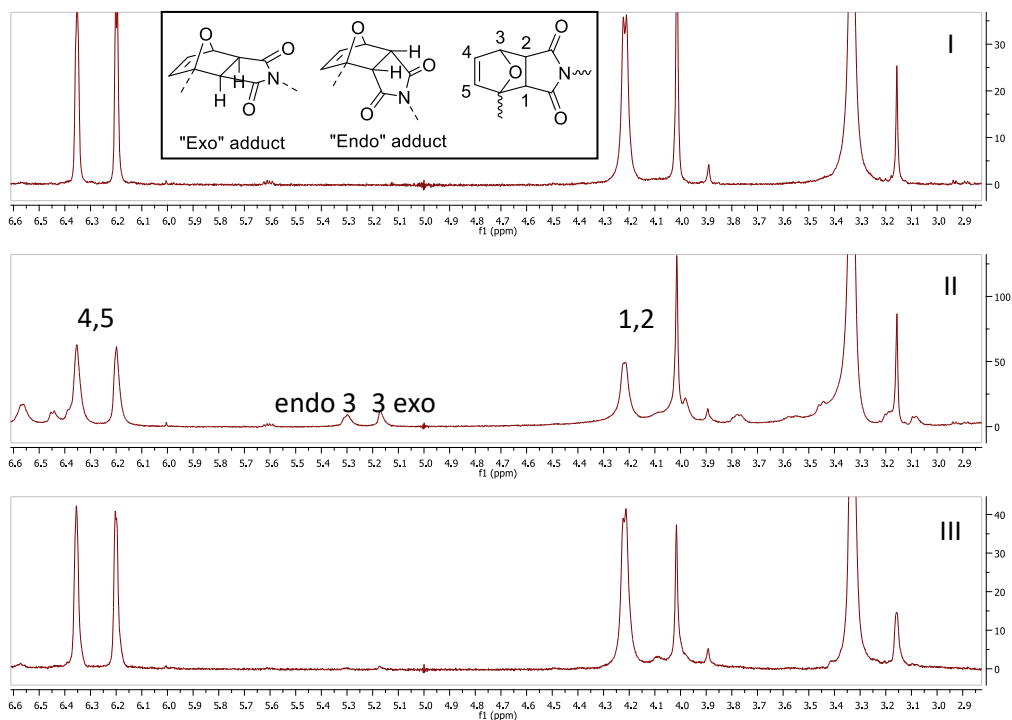


Figure 2: NMR spectra of uncrosslinked polymer and bismaleimide; I: no reaction, II: 3 h at 50°C, III: 5 min at 150°C. Inset: both regioisomers and assignments.

This is further proof, besides the gelation process and its reverse (*vide supra*), of the reversibility of this crosslinking system in solution.

Being able to observe the two DA adducts in the NMR, an attempt was made to quantify their relative ratio as function of temperature. This is quite interesting as such a shift in the ratio of these two adducts has been frequently invoked in literature in order to clarify the thermal behavior of thermal reversible networks^{12,35} and yet no clear proof has ever been reported for a crosslinked polymeric system. For the present system, in another experiment, the same solution containing uncrosslinked polymer and bismaleimide in a 1:1 maleimide:furan group ratio was created. A spectrum immediately after mixing was recorded (spectrum I in Figure 3). Next the sample was heated to 65°C for 2 h, and a new spectrum recorded (spectrum II in Figure 3). Once again the signals belonging to the DA adduct are found and the ratio of *endo:exo* adducts is 58:42. It is well known that the DA reaction is an equilibrium reaction, that the *exo* isomer is thermodynamically favored and the *endo* adduct is kinetically favored. When the sample is kept as 65°C for 48 h and another spectrum is recorded (spectrum III in Figure 3), the ratio of *endo:exo* isomers has shifted significantly to 11:88. This constitutes, to the best of our knowledge, the first direct confirmation of the two adducts formation in a as well as of their nature (thermodynamically and kinetically favored) for furan maleimide crosslinking reactions on a polymeric system. Indeed, other studies until now showed a similar behavior, but only model compounds or singular adducts have been used³⁶.

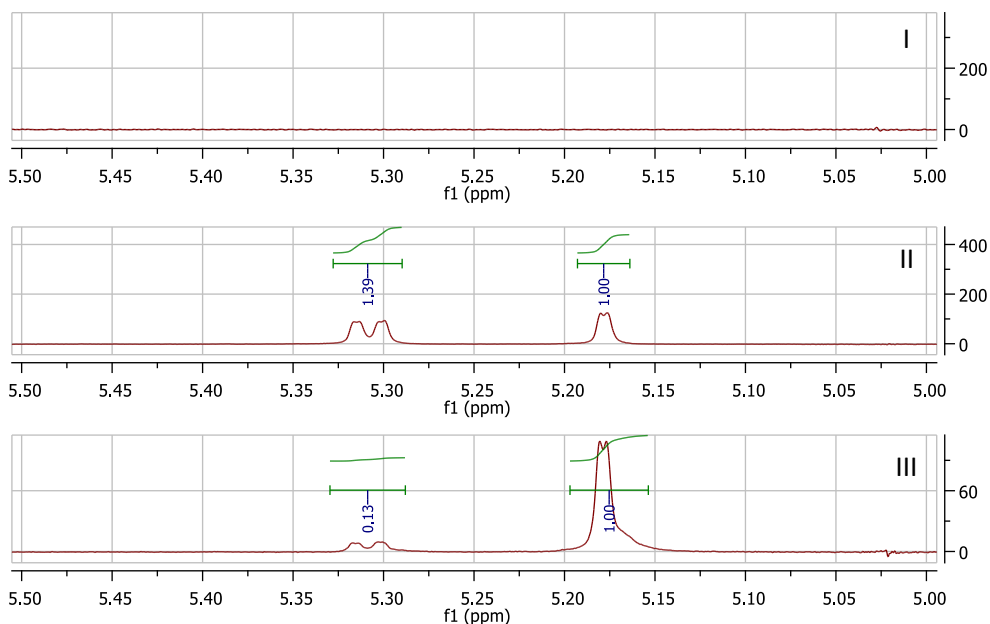


Figure 3: ^1H -NMR spectra of unreacted polymer and crosslinker (top) after 2 hours (middle) and 48 hours (bottom) at 65°C (only the endo/exo protons are shown)

The formation of the two DA adducts and their relative ratio might be of pivotal importance for thermal reversibility of the system, as suggested for related ones³⁷.

Thermal reversibility was tested by cyclical DSC measurements, according to which the material is heated to 180°C and subsequently cooled to room temperature for 8 consecutive times (Figure 4 for DPA-fur/tereph). The DA coupling is exothermic, while the RDA decoupling is an endothermic process. The integral of the corresponding peaks is an indication of the extent of the reaction.

The results suggest that the system shows thermoreversible coupling and decoupling: the heat capacity of the material does not change significantly over the course of all cycles, which is an indication of full reversibility^{12,37}. The peak at 150°C is related to the RDA decoupling reaction, while the DA coupling is not immediately apparent in this graph as it occurs gradually while cooling the sample. Over the course of all cycles, the maximum of the RDA peak at 150°C

shifts to higher values. A similar shift has been reported for related systems^{12,37}, for which this was firstly and hypothetically attributed to the RDA reaction being too slow with respect to the DSC timescale. However, this was later disproven and likely the difference lies in a change in the ratio of endo and exo DA-adducts. It has previously been established³⁸ that the exo isomer is thermodynamically favored, which makes it likely that the kinetically favored endo adduct is initially formed in excess. Nevertheless, during the course of heating and cooling this equilibrium shifts towards the more favored exo product, which in turn should have a higher temperature of RDA decoupling. This is in striking agreement with the NMR experiments (*vide supra*) and thus provides direct confirmation of the formation and importance of the adducts on the thermal behavior.

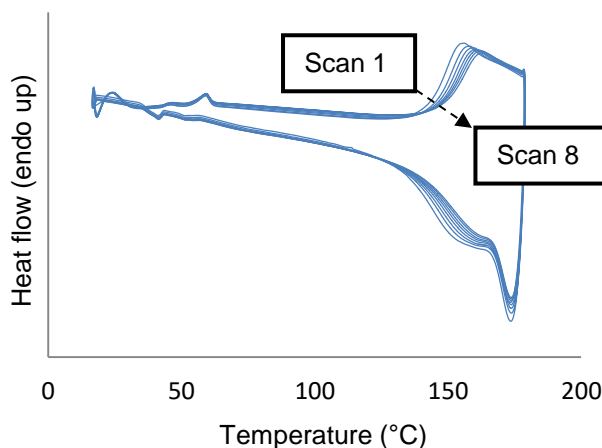


Figure 4: DSC measurements of reversible network formation for DPA-fur/Tereph

In order to assess the mechanical properties of the material, DMTA measurements were performed. The formation of solid, homogeneous bars is an indication of the reversibility of the compound, as without reversible crosslinking taking place only a compressed powder would be obtained. In order to elucidate the effect of the crosslinking degree on the softening temperature ($\tan(\delta)$ peak), various samples containing different maleimide:furan ratios were prepared. Figure 5 shows G' and G'' as well as the $\tan(\delta)$ for samples with 1:1 1:2 and 1:10 mol:mol ratios of maleimide:furan groups.

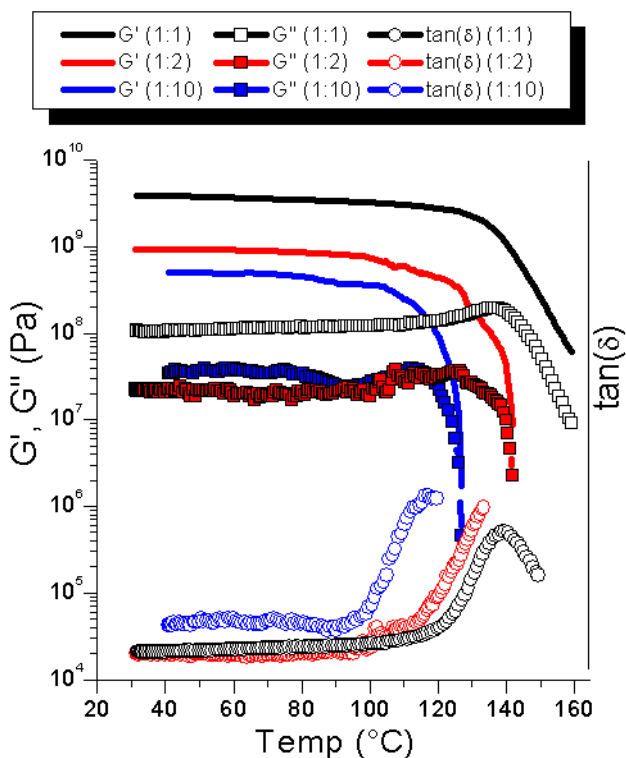


Figure 5: DMTA measurements of polymers containing various maleimide to furan ratios.

The softening temperature is 137°C, 135°C and 120 °C for the 1:1, 1:2 and 1:10 ratios of maleimide:furan respectively. The effect of the MAL:FUR ratio on the softening point is less expressed than that reported for related systems (Figure 6). A highly substituted (60%) polyketone-based system (PK50) displays a drop in softening temperature from 102°C to 86°C upon changing the MAL:FUR ratio from 1:1 to 1:2 (halving the amount of bismaleimide). An additional halving of the amount of bismaleimide leads to an even larger decrease of the softening point (22°C lower). A similar trend is observed when looking at the system obtained by the copolymerization of bis(hydroxymethyl)furane and succinic acid (PFS)³⁹: when halving the amount of bismaleimide the softening point drops from 38°C to 9°C. By noticing that this value is below the T_g of the uncrosslinked material (15°C)⁴⁰, the authors attribute this to a disturbance of the chain packing by the presence of crosslinker. For DPA-fur the effect of halving the amount of bismaleimide on the softening temperature is practically insignificant; only a drop of 2°C is observed.

Probably the large difference in softening point for the other systems stems from the low T_g of uncrosslinked polymer. When the amount of crosslinker is reduced, the material behaves more and more like a branched polymer structure than a three-dimensional network. The T_g of the material will become closer to that of the uncrosslinked polymer as fewer crosslinker is added. Interestingly, when reducing the amount of crosslinker even further to the ratio of 1:10 MAL:FUR the softening point of DPA-fur also drops below the T_g of the uncrosslinked polymer. The aromatic groups present in DPA-fur are likely involved in π - π stacking interactions which are disturbed by the presence of small amounts of crosslinker. Apparently the π - π -interactions have a larger influence on the softening point than the small amount of crosslinker present. Finally, the softening point observed for a 1:1 MAL:FUR DPA-fur network is much closer to the theoretical RDA temperature for furane and maleimide groups (e.g. 150⁴¹), which could be an indication of a more stable crosslink. Furthermore, as the material remains crosslinked for a larger range of temperatures (e.g. decrosslinking occurs at higher temperatures) this should provide a larger window of application for the resulting material than the PFS and PK50 based materials.

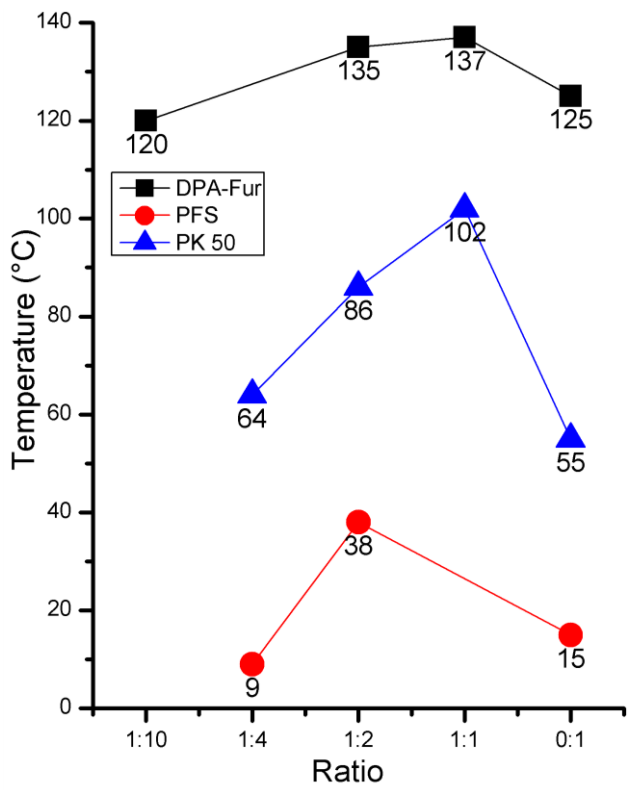


Figure 6: Softening temperature of various DA-systems for varying MAL:FUR ratios (0:1 refers to the uncrosslinked polymer)

Another way of influencing the thermal behavior is the use of a different crosslinker³⁹. When the aromatic bismaleimide was substituted by an aliphatic one containing a C12 chain between the maleimide groups, a drop of the softening point by 10°C was observed (Figure 7). These results are comparable to findings reported by Zeng *et al* where a drop of approximately 10°C was reported as well for the 1:2 ratio of MAL:FUR when substituting the aromatic bismaleimide for an aliphatic one containing a C₂OC₂OC₂ ether bridge⁴². This behavior likely comes from the increased flexibility of the aliphatic bismaleimide compared to its aromatic counterpart. This increased flexibility should result in a less rigid network. Furthermore, as suggested by the gelation experiments, the aliphatic crosslinker should be able to participate in backbiting coordination, limiting its availability for the formation of crosslinks. Independently of the exact mechanism, the observed results indicate that also in the case of the present polymer, the

amount and structure of the crosslinker might be conveniently used to manipulate the mechanical behavior of the end product.

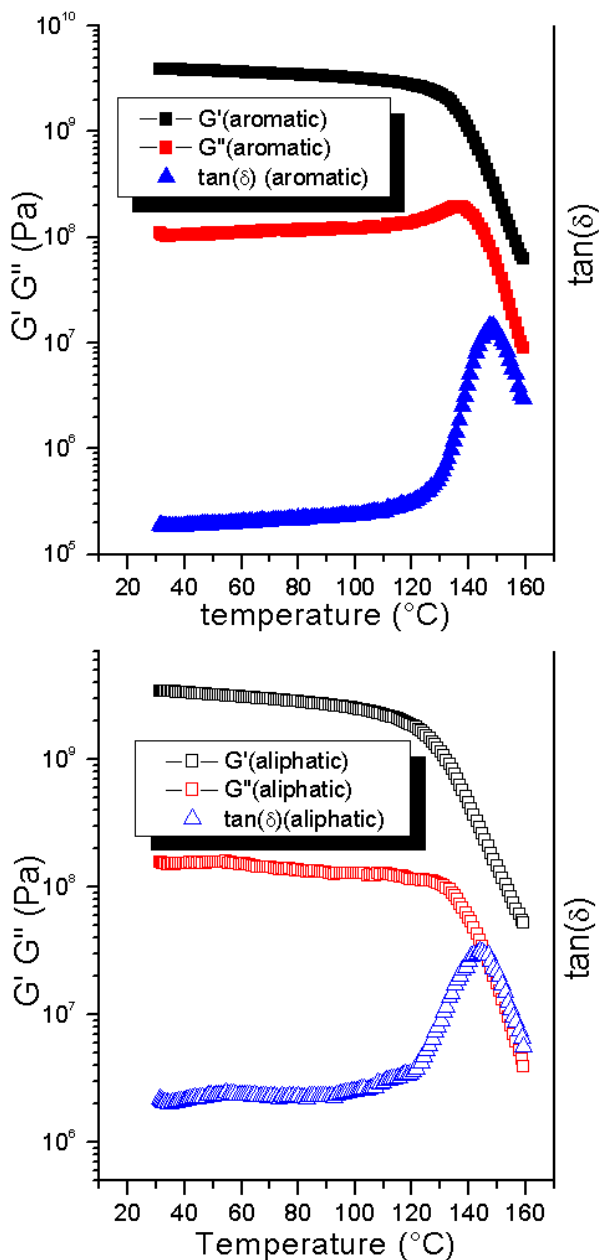


Figure 7 DMTA measurements of aromatic (top) and aliphatic (bottom) crosslinkers.

In order to assess the mechanical reworkability and thermal recovery of the material, cyclical DMTA measurements were performed. Samples were heated to 160°C and successively cooled back to room temperature (20°C) for 4 cycles (Figure 8). During cooling the material is expected to re-form the DA crosslinks which have been broken at high temperatures by the RDA reaction (which is dominant at these elevated temperatures). If the DA reaction is performed consistently, the material should display the same mechanical properties in all subsequent cycles. A relatively large change in properties is observed between the first and second cycle, this is consistent with the shift observed in DSC, and the explanation given of a kinetically favored orientation (endo vs exo) still holds true. However, after each consecutive cycle the softening point of the material increases. If the only equilibrium involved would be the changing from endo to exo isomer the difference should not be as large as observed. Most likely a more permanent change occurs in the material under these circumstances. A well-known side reaction of the Diels-alder adduct of furan and maleimide is the formation of an aromatic ring via the elimination of water⁴³. The mechanical properties of the material are not expected to change significantly in the low temperature region as in both cases (reversible crosslinked and aromatized crosslinked) a covalently crosslinked network is obtained. However, as the aromatization leads to an irreversible network under these conditions less crosslinks will be broken on each consecutive cycle explaining the ever increasing softening point. This indicates that the observed system is only able to display full reversibility for a few thermal cycles.

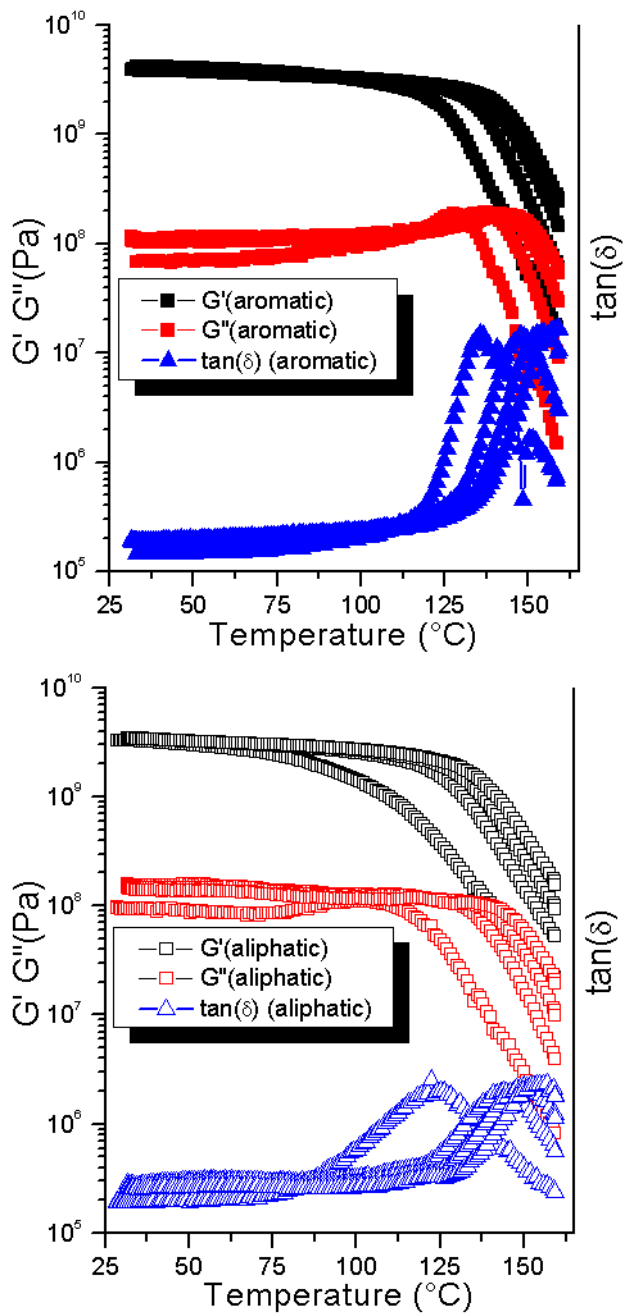


Figure 8: Cyclical DMTA measurements using the aromatic crosslinker (top) and the aliphatic crosslinker (bottom). Only the heating steps are shown.

2.5 Conclusions

In this work, diphenolic acid has successfully been functionalized with furfurylamine, yielding a furan-bearing diol. This has been incorporated into an aromatic polyester by reacting it with terephthaloyl chloride in an interfacial polycondensation reaction. The polymer obtained contains pendant furan groups which are able to participate in reversible crosslinking, forming a thermally reversible network.

Reversibility is shown in solution by gelation experiments where a gel is formed between 15 and 45 minutes when employing the aromatic crosslinker, depending on the ratio of maleimide to furan groups. Gelation with an aliphatic crosslinker takes significantly longer: 143 to 368 minutes, depending on the maleimide to furan ratio. Decoupling (evident by the transition of gel to solution) occurs for all samples in approximately 3 minutes at 150°C for all experiments.

Reversibility in the solid state is shown by cyclical DSC measurements where the peak for RDA decoupling has a maximum at 154°C for the first cycle. The maximum shifts slightly towards 160°C for the 8th cycle but all other thermal properties of the material remain constant. The small shift in the maximum is attributed to differences in the ratio of endo and exo adducts formed. NMR measurements showed a clear shift from a kinetic equilibrium to a thermodynamical one.

The material displays recovery of mechanical properties, as evident from cyclical DMTA measurements, after an initial change the polymer displays a high degree of recovery. However the increase in softening point after each cycle suggests that irreversible aromatization occurs of the furanes and maleimides.

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Chapter 3

The effect of molecular weight on the (re)-processability and material properties of bio-based, thermoreversibly cross-linked polyesters

3.1 Abstract

A (partially) bio-based short-chain polyester is prepared through interfacial polycondensation of furan-functionalized diphenolic acid with terephthalic chloride. The furan groups along the backbone of the obtained polyester are able to form a covalent network (PE-fur/Bism) with various ratios of 1,1'-(methylenedi-4,1-phenylene)bismaleimide via the thermoreversible Diels-Alder (DA) reaction. Several techniques have been employed to characterize the polyester network, including: $^1\text{H-NMR}$, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The polyester base polymer displays a glass transition temperature of $115\text{ }^\circ\text{C}$ while the temperatures at which the retro-Diels-Alder (rDA) reaction takes place lie above $130\text{ }^\circ\text{C}$ for the various polyester/bismaleimide networks. Excellent thermoreversibility and recyclability of the polyester resin have been shown through DSC and DMTA measurements.

Keywords: polymers, bio-based, short-chain, polyester, furan, bismaleimide, thermoreversibility, Diels-Alder, recyclability.

3.2 Introduction

In the past 20 years the focus in the field of research on polymeric products has shifted towards the synthesis and application of polymers which are both bio-based and recyclable¹. In the near future this will become even more important due to the growing scarcity of petroleum as a feedstock for current conventional polymeric products. Various publications describe the successful substitution of petroleum-based components with bio-based analogues²⁻⁵. However, to produce a sustainable product it is of vital importance not only to focus on the feedstock materials, but also to look at what is done with the product after utilization (i.e. the waste generated at end of life). It is well-known that recyclability of polymeric systems in general, and thermosets in particular, is often still a challenge^{6,7}. The permanent shape and structure imparted by the covalent crosslinks severely limits the reusability of these polymers⁸, which undergo degradation (as opposed to the desired softening or melting) upon heating.

There is no viable, straight-forward replacement for thermoset materials as the (densely) crosslinked networks of these materials impart superior barrier and

mechanical properties compared to their (non-crosslinked) thermoplastic analogues. Due to this durable nature, thermosets are often used in a wide variety of applications such as composites, adhesives and coatings. The downside of these strong, (densely) crosslinked networks, however, is that thermosets do not possess the chain mobility that thermoplastics often do. This severely reduces their (re)processability and intrinsic capability to be repaired⁹. As a consequence, many thermoset resins cannot be recycled after usage and eventually end up in landfills. In recent years, the laws for waste management have become stricter, placing ever more emphasis on the production of recyclable products. Preventing waste at the source of manufacture is the most desired way to manage waste¹⁰. There are various ways of interpreting these goals. Enabling recyclability of previously unrecyclable materials reduces the demand for the production of new material, effectively preventing waste at the source. For polymer thermosets, one of the options to achieve this is to introduce thermoreversibility into the polymeric material, namely as characteristic feature of the crosslinking reaction. This thermoreversibility gives rise to the possibility of remolding and reshaping the thermoset material by applying heat, while optimally the mechanical properties of the material are retained.

One way to introduce thermoreversible crosslinking into a polymeric system is to incorporate moieties that are capable of undergoing (reversible) Diels-Alder interactions. Once incorporated into the polymer matrix these moieties can act as crosslinking points. The general Diels-Alder mechanism consists of a $(4\pi + 2\pi)$ cycloaddition reaction between a conjugated diene and an alkene as dienophile to form a (substituted) cyclohexene system¹¹⁻¹³. This cycloaddition leads to the formation of covalent bonds at lower temperatures (generally around 50 °C and below) through the Diels-Alder (DA) reaction, while, the reaction being an equilibrium, at higher temperatures (approximately 120 °C and above) the covalent bonds break and the original diene and dienophile groups are obtained through the retro-Diels-Alder (rDA) reaction¹⁴. The first preparation of thermally reversibly crosslinked polymers employing DA chemistry was reported by Craven *et al.*^{6,15}. A furan-functionalized polymer is described, which forms thermally reversible networks with multiple maleimides. A large number of diene and dienophile couples can be used in DA chemistry, where electron-pushing and electron-withdrawing substituents in the diene and dienophile greatly influence

the reactivity¹⁶. The furan ring is one of the most important dienes used in DA reactions, due to the exceptional dienic character of the furan ring, which makes it specifically suitable in terms of kinetics and yields¹⁷. On top of that, furan compounds are often obtained from renewable sources. Furthermore, maleimides are commonly used as dienophilic counterparts because of their highly reactive nature due to electron-withdrawing substituents adjacent to the double bond¹⁷. The coupling (DA) and decoupling (RDA) temperatures for the furan maleimide pair (~50°C and 150°C respectively) make this couple very suited for this application. Finally, the Diels-Alder reaction can be performed without solvent and does not need a third chemical such as a catalyst to function¹⁸⁻²⁰. If this mechanism would be used as a crosslinking system in thermoset polymers it would greatly increase the mobility of the chains at higher temperatures. (i.e. above the RDA temperature) When the rDA temperature is below the degradation temperature of the material or in general the temperature at which side-reactions occur, the polymeric system is regarded as fully thermoreversible. An important element in the concept of thermoreversible crosslinking is that often not all the crosslinks have to be broken for the system to be recyclable, as long as the extent of bond breakage results in a flowable polymer melt¹⁸. Thermoreversible systems employing Diels-Alder cross-linking chemistry give rise not only to improved processability and recyclability, but also to very specific and novel, unique applications such as self-healing/remendable polymers^{6,14,20-25}, shape-memory materials^{7,26}, probe-based lithographic and data-storage applications²⁷, removable foams for electronic encapsulation²⁸, thermally reversible gels^{29,30}, polymeric encapsulants²² and thermally removable adhesives³¹.

In this work, the preparation and characterization of a (partially) bio-based thermoreversible polyester resin is discussed. One of the main building blocks of this polyester is diphenolic acid, which can be derived from the bio-based building block levulinic acid³². Diphenolic acid is an acid-functionalized structural analogue of bisphenol A (BPA), which is widely used for commercial polycarbonate, epoxy and polyester resins^{33,34}. The acid functionality of diphenolic acid is further functionalized with a furan group, introducing a Diels-Alder capable moiety. Finally, a polyester base-polymer is obtained via interfacial polycondensation of the furan modified diphenolic acid and terephthaloyl chloride, using phenol as a chain stopper (PE-fur, Figure 1). The addition of chain stopper should lower the

average chain length of the polymer obtained, which in turn should reduce the glass transition temperature (T_g) of the material. This reduction is needed because it has been demonstrated that the T_g of PE-fur (without chain stopper) is too high for processing (e.g. the required processing temperature in order to assure proper polymer flow is too close to the degradation temperature)³⁵. Phenol is of particular interest since it conserves aromaticity, readily takes part in the condensation synthesis and shares a structural similarity with diphenolic acid. Furthermore, it can be obtained from bio-based sources^{36,37}.

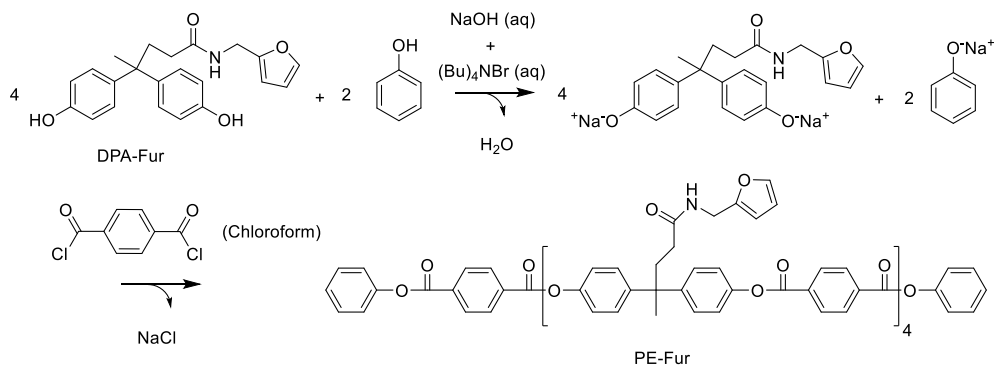


Figure 1: Synthesis of PE-fur from furan-functionalized diphenolic acid

3.3 Experimental section

3.3.1 Materials and reagents

Phenol ($\geq 99\%$, Sigma-Aldrich), tetra-*n*-butylammonium bromide ($\geq 98\%$, TBAB, Fluka), terephthaloyl chloride ($99+\%$, Acros), NaOH (97% , Sigma-Aldrich), methanol (practical grade, Interchema), chloroform (anhydrous, $\geq 99\%$ Lab-Scan), and 1,1'-(Methylenedi-4,1-phenylene)bismaleimide (95% , Bismaleimide, Sigma-Aldrich) were used as received. DPA-fur was prepared following a reported procedure¹.

3.3.2 Characterization

¹H-NMR spectra were taken on a Varian Mercury Plus NMR-300 and a Varian Mercury Plus NMR-400 using DMSO-*d*₆ as a solvent. GPC measurements were performed on a HP1100 equipped with three 300x7.5 mm PLgel 3 μ m MIXED-E columns in series using a GBC LC 1240 RI detector. Average molecular weight

calculations were performed with the PSS WinGPC Unity software from Polymer Standards Service. The following conditions were used: THF as eluent at a flow rate of 1 ml min⁻¹; 140 bar, a column temperature of 42 °C, 20 µl injection volume and a 10 mg mL⁻¹ sample concentration. Toluene was used as a flow marker and polystyrene samples with different molecular weights were used as calibration standard. DSC data was recorded on a Perkin Elmer DSC Pyris 1 from 20 °C to 180 °C at rates of 2 °C/min or 10 °C/min. TGA data was recorded on a Mettler Toledo TGA. DMTA measurements were performed on a Rheometrics scientific solid analyzer (RSA II) under air environment using a dual cantilever at an oscillation frequency of 1 Hz and a heating rate of 2 °C/min. The data was measured during four cycles in a temperature range of 20 °C to 160 °C.

3.3.3 Synthesis of polyester-furan

The reaction of the DPA-fur monomer with terephthaloyl chloride results in a polyester containing pendant furan groups. The ratio of monomer/chain stopper added in this reaction was set at 4:2 to yield an average theoretical chain length of four monomeric repeating units, end-capped by two chain stoppers.

5.00 g (13.8 mmol, 4 eq.) DPA-fur, 0.435 g TBAB (8.7 %wt of DPA-fur), 0.644 g (6.841 mmol, 2 eq.) phenol, 1.411 g (34.2 mmol) NaOH and 120 mL water were added to a 500 mL round bottomed flask. Subsequently, the reaction was stirred for 2 h at room temperature. Afterwards, 3.125 g (15.39 mmol) terephthaloyl chloride dissolved in 120 mL chloroform was added to the mixture. The reaction mixture was then stirred overnight at room temperature. Finally, the polymer was precipitated in a large beaker containing 2 L methanol. The precipitation yielded a solid precipitate on the bottom of the beaker, as well as a suspension of small particles in the methanol phase. The methanol phase containing small solid particles was centrifuged in 50 mL cups at 4500 rpm for 15 min. Furthermore, the precipitate obtained in the centrifuge cups was filtered over a Büchner funnel and washed with 50 mL of water. Additionally, the solid precipitate on the bottom of the beaker was also filtered over a Büchner funnel and washed with water. Finally, all the solid products obtained were combined and dried in an oven at 70 °C for a couple of hours to yield a white-yellowish solid (PE-fur, best yield achieved 74%).

¹H-NMR (300 MHz, DMSO-d₆): δ = 8.32-8.10 (m, 7H, aromatic not next to ester), 7.55 (s, 1H, fur-p), 7.49 (d, 1H, NH), 7.4-7.2 (m, 8H, aromatic next to ester), 6.37
70

(s, 1H, fur-m), 6.22 (s, 1H, fur-o), 4.23 (d, 2H, N-CH₂), 2.43 (s, 2H, -CH₂-), 1.98 (s, 2H, -CH₂-), 1.66 (s, 3H, -CH₃).

3.3.4 Preparation of polyester-furan/bismaleimide networks

The PE-fur/Bism networks were prepared via a general method. An amount of PE-fur (1.00 eq. mol) was added to a single-neck round-bottomed flask. The molar amount of furan groups was estimated by assuming that the polymer consists only out of monomeric repeating units with a molecular weight of 496.53 g/mol (1 DPA-fur group and 1 terephthaloyl group, see Figure 1). This was assumed in order to calculate the molar amount of maleimide groups needed.

Subsequently the proper amount of bismaleimide was added, different ratios were used to create different networks (0.50 eq. mol, 0.25 eq. mol and 0.125 eq. mol bismaleimide with respect to the furan content). While the mixture was stirred at 60 °C, just enough chloroform was added to dissolve the PE-fur and bismaleimide in order to create a homogeneous mixture. The chloroform was then partially removed by rotary evaporation (40 °C, 800 mbar) to yield a dark-brown rubbery substance. Completely removing the solvent by rotary evaporation is not recommended as this results in a hard yellowish/brown product, which is hard to remove from the glassware.

The dark-brown rubbery substance was ground using a motorized hand grinder, and subsequently dried in a vacuum oven (10 mbar, 45 °C). Finally, the resulting product was ground in liquid N₂ with a motorized hand grinder to yield a fine light-yellow powder (PE-fur/Bism) in quantitative yield.

3.3.5 Preparation of DMTA specimens

DMTA specimens were obtained by hot compression-molding of a mixture of PE-fur/Bism into bars with dimensions of 54x6x1 mm (length, width, height). The pressing sequence consisted of first cold pressing the polymer in the mold for 2 minutes at room temperature and 10 MPa. Subsequently, the polymer was pressed in a pre-heated press for 2 h at 150 °C and 10 MPa. The press was then slowly cooled down to 50 °C, after which the DMTA bars were treated at 50 °C for 24 h. Specimens from different molar ratios of furan/bismaleimide have been prepared: 2:1, 4:1 and 8:1.

3.4 Results and Discussions

The addition of a chain stopper appears to have little effect on the polymerization reaction kinetics. The reaction still proceeds readily as is evident from comparable yields in identical reaction conditions. There is, however, a small negative impact on total yield: the precipitation step does not yield all the polymer as the molecular weight of the shortest fractions is limited and as such they are still soluble in methanol. Furthermore, there is a very clear effect on chain length as shown in GPC elugraphs. A significantly shorter polymer is obtained when comparing the obtained PE-fur with the long chain PE-fur described before ¹ (Figure 2).

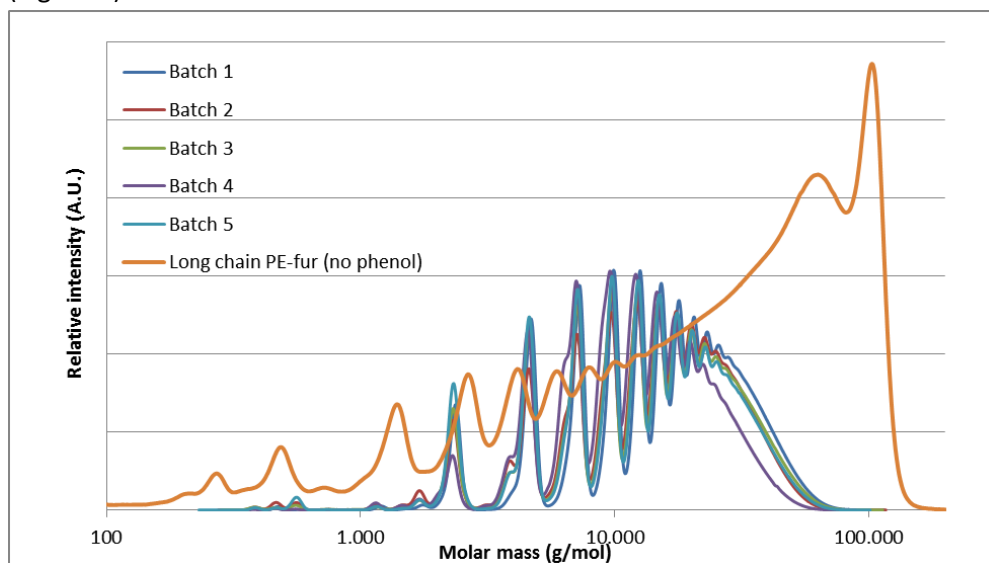


Figure 2: GPC spectrum of multiple PE-fur batches.

First, the presence of multiple peaks instead of a single smooth curve indicates that the sample consists of relative small polymers containing relatively large monomeric repeating units. This is also reported for the synthesis of cyclic polycarbonates from various bisphenol analogues³⁸⁻⁴⁰. The difference in molar mass between the various peaks is more or less the same, ranging from 2300 g/mol to 2700 g/mol. Both the height and narrow appearance of the peaks, as well as the more or less constant difference in molar mass between them are strong indications for the presence of short-chain polyesters with each peak varying one monomeric repeating unit from its neighbor. The successful

application of phenol as chain stopper is evident from the elugrams of both polymers, comparing the long-chain polyester to the short-chain one (Figure 2) the latter obviously has a lower average M_w . The large peak at 200,000 g/mol in the long chain PE-fur results from the limitations of the column used, and it contains all fractions with higher M_w as well.

Differential Scanning Calorimetry was used to determine the processability of the polyester as well as the thermal reversibility of the polyester/bismaleimide networks. The glass transition temperature of PE-fur lies around 115 °C (Figure 3a). The long-chain polymer made without the use of phenol possesses a T_g of approx. 125 °C¹. The effect of shortening the polymer chains by employing phenol as a chain stopper has led to a decrease of approximately 10 °C in T_g . The decrease in T_g with decreasing chain lengths is also seen for other linear bisphenolic polymers^{41,42} and can primarily be ascribed to the loss of entanglements due to the shortening of chains (Figure 3).

When the temperature increases above 130 °C a transition takes place, which corresponds to the rDA reaction^{7,9,22}; as evident from the peak in the DSC spectrum. This is observed in all of the three different resins and in all of the heating steps. Subsequently, during cooling down an exothermic peak is shown in the same region, indicating the occurrence of the DA reaction²². The position of the endothermic peak of the first cycle appears to differ from the subsequent cycles (most clearly observed in Figure 3b and d). This phenomenon has previously been reported for a furan/maleimide polyketone network²⁶ and a thermoreversible epoxy resin^{23,43}. The shift of the endothermic peak to higher temperatures might be explained by the transition of DA adducts from the *endo* to the *exo* conformation^{1,44}. The enhanced thermodynamic stability of the *exo* adduct explains the shift of the peak towards higher temperatures after the first cycles²⁶. Although the next cycles appear to be very similar, a slight decrease in the peak area of the DA peak is observed. This may be due to the fact that the system does not have enough time to fully recover all the DA bonds^{6,26} or that the *endo/exo* equilibrium is still shifting towards the more stable *exo* adduct¹. The equality of the subsequent thermal cycles is a strong indication of thermoreversibility.

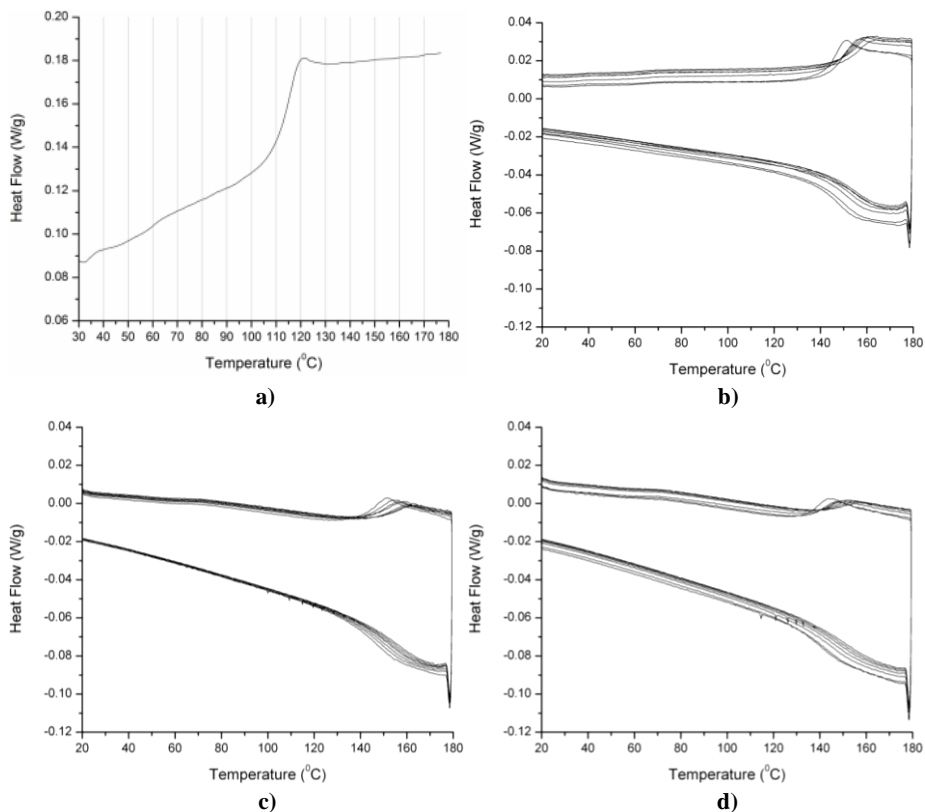


Figure 3: DSC measurements of:

(a) Tg of PE-fur. (b) PE-fur/Bism-2:1. (c) PE-fur/Bism-4:1. (d) PE-fur/Bism-8:1.

When comparing the different composition ratios of the polyester resin, the integral of the peak around 140 to 160 °C corresponding to the rDA reaction decreases in the line of PE-fur/Bism-2:1 > 4:1 > 8:1. This result confirms that lowering the amount of crosslinker reduces the amount of coupled groups and subsequently the energy needed to decouple them. This has also been reported for other systems with fixed furan content and lower crosslinking concentrations²⁶. Furthermore, the temperature at which the rDA reaction occurs only changes marginally for other composition ratios of the polyester and bismaleimide, which is in agreement with reports on other furan/bismaleimide networks²⁶.

$^1\text{H-NMR}$ was employed to give more insight into the stereoselectivity of the DA reaction. It is well known that the DA reaction of furan and maleimide forms a stereoisomeric mixture. Initially the kinetically-favored *endo* adduct is formed, though at higher temperatures the thermodynamically favored *exo* conformation is obtained⁴⁵⁻⁴⁷. Hence, after heating the material above the rDA temperature, the more stable *exo* adduct will mainly be formed upon cooling down from a high temperature starting point. The DSC results indicate that after multiple heating cycles the conformation of the formed adducts gradually shifts from *endo* to *exo*, resulting in a higher thermal stability of the adducts. As evident from the shifting of the DSC RDA peak to higher temperatures. The shift from *endo* to *exo* configuration at higher temperatures is confirmed by multiple sources⁴⁵⁻⁴⁹, often accompanied by NMR studies on model compounds. Figure 4 shows NMR spectra of PE-fur and bismaleimide after several stages.

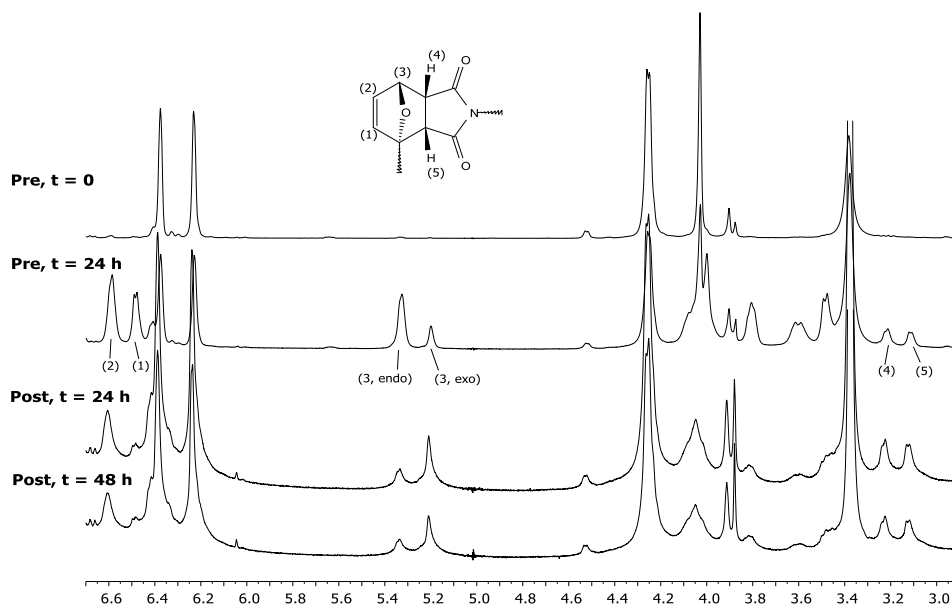


Figure 4: $^1\text{H-NMR}$ spectra of PE-fur/Bism recorded at various moments before and after heating.

First, a 10 %wt amount of PE-fur and bismaleimide was dissolved in DMSO-d_6 in a teflon capped NMR-tube. The first spectrum was recorded directly after mixing, (Figure 4top (Pre, t = 0)). Subsequently, the NMR tube was kept at room temperature for 24 hours; during this time a gel was formed, indicating crosslink

formation via the DA reaction. Then the next spectrum was recorded (Figure 4 (Pre, t = 24 h)). The NMR tube containing the gelled sample was heated at 120 °C for 30 min in a NMR-tube oven, after which the oven was switched off. The sample was kept in the oven for 24 hours, in order to slowly cool down the sample to room temperature. (Figure 4 (Post, t = 24h)). Finally, the last spectrum was recorded after keeping the sample at room temperature for another 24 hours, (Figure 4 (Post, t = 48 h)).

Multiple peaks corresponding to protons in the Diels-Alder adduct can be observed in the ¹H-NMR spectra. The peaks belonging to the proton that is adjacent to the adduct bridge are most clearly differentiated from the others. It is known from literature that the peaks around δ 5.2 and δ 5.3 ppm belong to this adjacent bridge proton and correspond to the *exo* and *endo* conformations, respectively^{6,17,50}.

It was found that initially (at t = 0 h) no adduct protons are present, showing that the DA reaction has not yet taken place. After 24 h at room temperature, the adduct formation is indicated by the appearance of multiple peaks (Figure 4, Pre, t=24h, peaks 1-5) corresponding to the DA adduct^{6,14,17}. The intensity of the peak at δ 5.33 ppm (3), corresponding to the *endo* conformation, is much larger than that of the peak at δ 5.20 ppm (3), corresponding to the *exo* conformation. The ratio of *endo/exo* conformations after 24 hours at room temperature is 77%/23% respectively. After heating to 120 °C and cooling down for respectively 24 and 48 h ¹H-NMR peaks are again observed that correspond to the DA adduct. However, when comparing the *endo/exo* ratio to the gel obtained at room temperature, after heating the integral of the *exo* peak is larger; the ratio of *endo/exo* after 24 and 48 h post-heating is 32%/68% respectively. The fact that the spectra recorded after 24 and 48 h post-heating are identical indicates that equilibrium conditions in DA adduct formation are reached within the first 24 hours or that the adduct is stable at room temperature. It is worth noting that multiple reactions can occur in a small temperature window close to the rDA temperature: adduct formation via the DA reaction, adduct breakage via the rDA reaction and isomerization of the *endo* to the *exo* adduct⁵⁰. The results obtained via the NMR experiments would indicate that the shift in the ratio of *endo/exo* conformations after a heating cycle confirms that the *exo* conformation is indeed favored at higher temperatures. This further justifies the conclusions drawn from the DSC spectra. Differences in

thermal reversibility due to the influence of either *endo* or *exo* adducts can have an important impact on the material properties of especially thermoremendable polymers and networks⁵¹. The influence of stereoselectivity on the mechanical properties of the prepared polyester resin were examined and will be discussed later on (*vide infra*). The first (strong) indication of thermoreversible crosslinking is the ability to produce homogeneous test-specimens using hot compression-molding from material that already was crosslinked in solution. This would not have been possible using material containing non-reversible crosslinks, as the final material would be a sintered compressed powder²⁶.

Firstly, it is observed that during the first cycle, E' and E'' drop at elevated temperatures (most clearly seen for ratio 2:1, Figure 5). This is due to buckling of the bars as a result of the sideway forces exerted by the DMTA-machine sample holder. At elevated temperatures (starting from 132 °C for ratio 2:1 and 114 °C for ratio 4:1) a large decrease in moduli is observed, it is also in this region that $\tan \delta$ increases rapidly (Figure 5a, b and c). This change is due to the DA-rDA equilibrium that shifts to favor the rDA reaction. This results in decrosslinking in the polymer resin. This yields a softening point at elevated temperatures after which the polymer exhibits viscous behavior, rather than elastic⁵². During the multiple DMTA-cycles the mechanical properties remain the same in the glassy region, while the temperature of the softening point shifts to higher values after each cycle. The shift of the softening point has previously been attributed to an increase in crosslink density²¹. However, recent publications attribute this to the change in conformation of the DA adduct from *endo* to *exo*⁵³. Since the *exo* adduct is more thermally stable, a shift of the softening point to higher temperatures seems logical. The change in softening temperature implies that the rDA reaction becomes more difficult (due to the fact that the adduct becomes more stable) after multiple heating cycles⁵³.

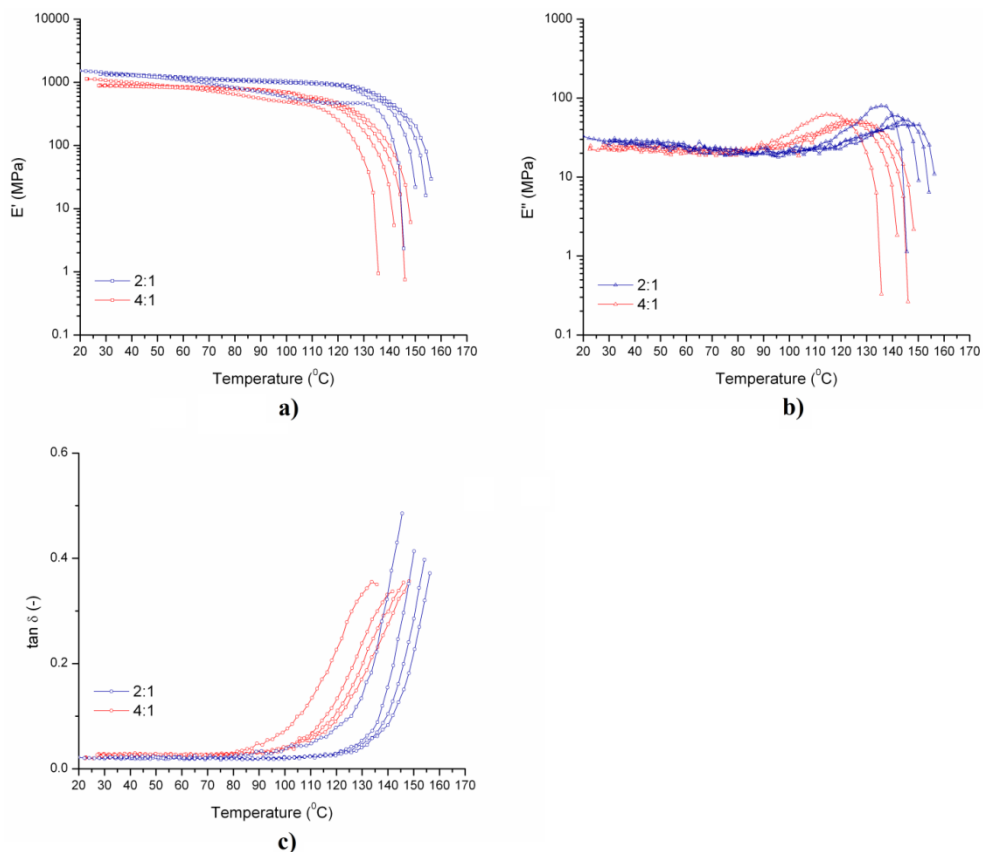


Figure 5: DMTA of various specimens of PE-fur/Bism (a) Storage modulus E' . (b) Loss modulus E'' . (c) Damping factor $\tan \delta$. Only the heating steps are shown for clarity

When comparing the mechanical properties for different ratios polyester/crosslinker, a slight decrease in the storage modulus (E') is observed for the ratio of 4:1 (polyester/bismaleimide) with respect to 2:1. The maximum of $\tan \delta$ also slightly shifts to a lower temperature. Similar material response upon varying the furan/maleimide ratios was also observed for other furan/maleimide systems^{6,26}. The stiffness of the polymers generally decreases with the crosslink density^{6,54-56}. The loss moduli (E'') for the various ratios are more or less similar at lower temperatures, though here also a ratio dependent softening temperature is observed. The softening points of the different samples are 146 °C and 136 °C for PE-fur/Bism-2:1 and -4:1 respectively. The softening points are determined from the points of maximum decrease of the storage moduli during the first cycles. In a previous publication describing¹ measurements on long-chain PE-fur/Bism

networks comparable softening points have been reported: 138 °C and 136 °C for furan/bismaleimide mixtures with 2:1 and 4:1 molar ratios respectively. Thus, it can be concluded that the addition of chain stopper has had a negligible effect on the stability of the polymer network.

A life-cycle of the test-specimens prepared from PE-fur/Bism shows newly compression molded bars prepared according to the method described in the experimental section (Figure 6). After a four cycle DMTA experiment (20°C-160°C-20°C) an optical change in the appearance/shape of the bars was visible (Figure 6b): the test-specimens have buckled under the force exerted during the DMTA measurement. Furthermore, a change in color is observed, changing from dark yellow before the DMTA to brown afterwards. Since no antioxidants had been added, this color change may be caused by oxidation of the material. Analysis of the material by NMR and IR however, showed no (significant) formation of side products, nor any indication of degradation.

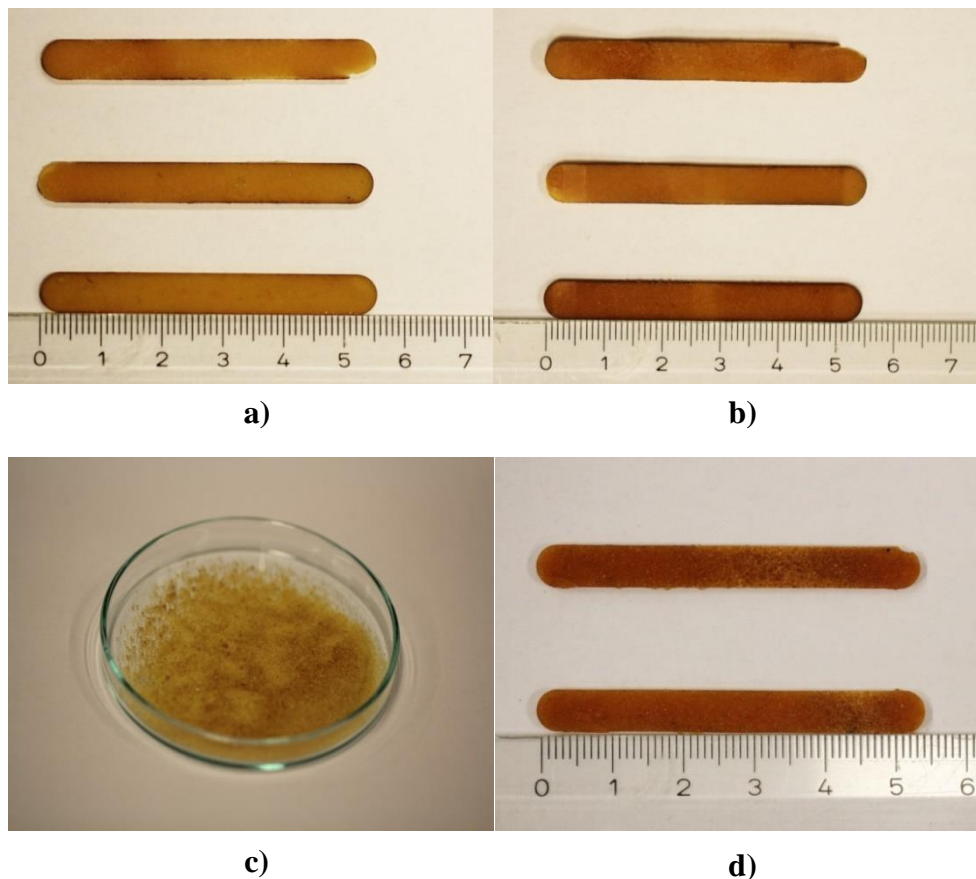


Figure 6: Bars prepared from PE-Fur/Bism (a) Hot-pressed PE-Fur/Bism bars. (b) PE-Fur/Bism bars after 4 DMTA Cycles. (c) Reground PE-Fur/Bism bars after DMTA. (d) Recycled PE-Fur/Bism bars.

After measuring, the bars were reground into powder using a motorized hand-grinder (Figure 6c). Ultimately, the reground powder was again processed into DMTA bars via the same compression molding procedure (Figure 6d). These resulting, recycled PE-fur/Bism bars display an even darker brown color in comparison to the dark-yellow and light-brown colors seen in Figure 6a and b respectively. Analysis of the reprocessed material still indicated no impurities. As noted, the coloring is likely due to the formation of very small amounts of highly colored products that are undetectable by $^1\text{H-NMR}$. This life-cycle sequence of PE-fur/Bism test-specimens emulates the ultimate goal in terms of thermoreversibility: recycling polyester resin material after usage.

A temporary decrease of the storage and loss moduli is also visible during the first DMTA cycle of the recycled test bars due to buckling of the test specimen (Figure 7), as a result of the sideways forces exerted by the DMTA-machine sample holder.

In contrast to the virgin PE-fur/Bism-2:1 material, it is seen that the recycled material exhibits a slightly lower storage modulus and loss modulus, indicating somewhat less mechanical strength. However, this difference is only marginal and proofs that even after complete recycling, the mechanical properties are still equivalent.

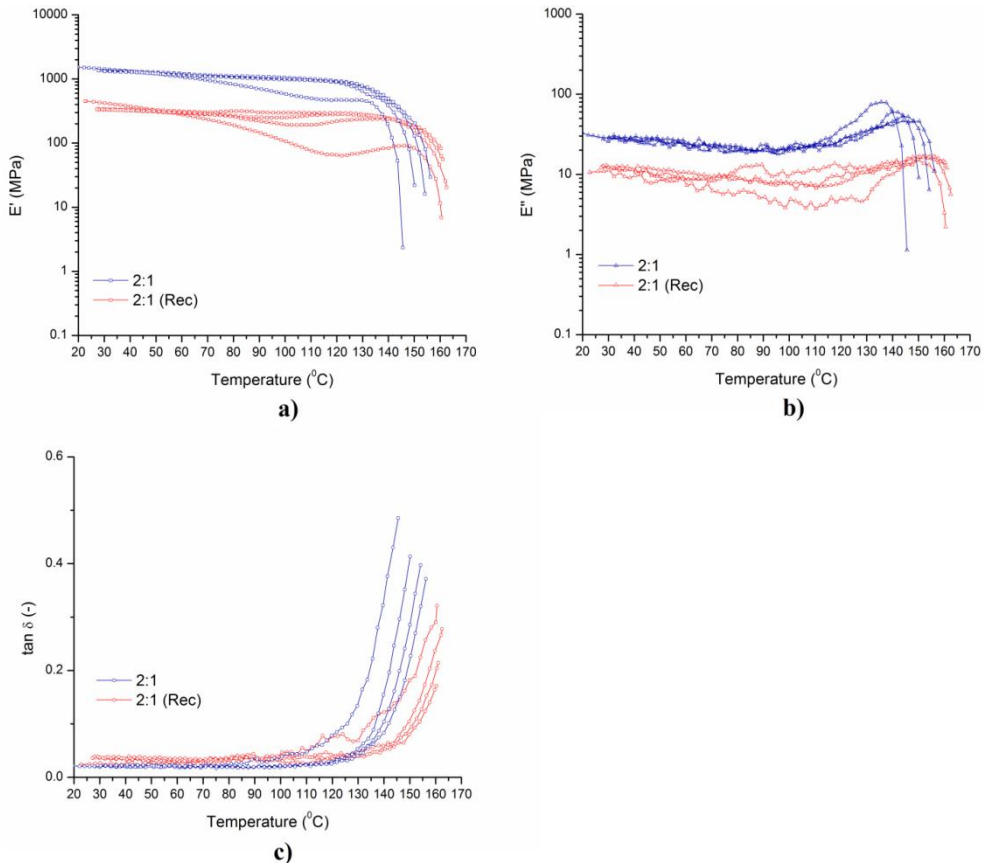


Figure 7: Dynamic Mechanical Thermal Analysis of recycled specimens of PE-fur/Bism (a) Storage modulus E' . (b) Loss modulus E'' . (c) Damping factor $\tan \delta$

The same phenomenon described earlier (the shift of the softening point to higher temperatures after each cycle) is also observed for the recycled polyester

resin. This, again, suggests increasing difficulty for the rDA reaction to occur after multiple heating cycles, possibly due to conformational changes of the adducts resulting in DA adducts with higher thermal stability. (e.g. from *endo* to *exo*¹)

When comparing the softening temperatures of the newly prepared test-specimens with those of the recycled ones, it is seen that the softening points of the recycled specimens lie at higher temperatures. Since the recycled test specimen has been exposed to more heating cycles than the virgin material has, it is fair to assume that the recycled polyester network possesses a relative higher amount of thermally stable adducts. Again, this ultimately results in increased temperatures needed to induce the rDA reaction. This phenomenon, however, does not seem to have any significant effect on the mechanical properties of the material.

The mechanical properties of the recycled material are unchanged throughout the subsequent DMTA-cycles. This shows that the recycled material does not yield poorer mechanical properties, even after multiple measurements at various temperatures. Ultimately, the fact that the mechanical properties of the virgin and the recycled PE-fur/Bism material are comparable indicates that this indeed constitutes a fully thermoreversibly recyclable polymer.

3.5 Conclusions

A (partially) bio-based, short-chain polyester has been synthesized to incorporate furan moieties that are capable of undergoing Diels-Alder reactions with bismaleimide crosslinkers. This polyester possesses a lower glass transition temperature than the long-chain polyester described¹ previously (i.e. 115 °C versus 125 °C), which results in improved processability.

The short-chain, furan-functionalized polyester has been reacted with bismaleimide which acts as a crosslinking agent, yielding a thermoreversible covalent network through the Diels-Alder reaction. The mechanical properties of the network have been influenced by varying the ratio of crosslinker versus furans. A decrease in softening point from 146 to 136 was observed upon halving the amount of bismaleimide. Thermoreversibility was shown by cyclic DSC measurements as the observed transitions during heating and cooling correspond to the rDA and DA reactions respectively. The small variations observed between

subsequent cycles are attributed to the transition of the DA adducts from the *endo* to the *exo* conformation, these variations are confirmed by $^1\text{H-NMR}$ measurements which shows that initially the *endo* adduct is favored during room temperature crosslinking in solution. Subsequently exposing the solution to elevated temperatures ($120\text{ }^\circ\text{C}$) shows preferred formation of the *exo* adduct.

DMTA measurements also show thermoreversibility of the polyester resin during multiple cycles of measurements in a temperature range of $20\text{ }^\circ\text{C}$ to $160\text{ }^\circ\text{C}$. The mechanical properties of the examined polyester networks remained identical during the multiple cycles even after the thermally induced softening of the material due to the rDA reaction and accompanying decrease of mechanical properties at temperatures above $110\text{ }^\circ\text{C}$ apart from a minor shift in softening point due to the aforementioned *endo-exo* isomerism. When changing the molar ratio of furan:maleimide from 1:1 to 2:1 respectively, a decrease in softening point is seen (from $146\text{ }^\circ\text{C}$ to $136\text{ }^\circ\text{C}$) as well as a decrease in storage modulus, indicating a less densely crosslinked network with poorer mechanical properties for lower amounts of crosslinker. This is supported by the fact that proper test-specimens for the furan:maleimide ratio 4:1 could not be obtained due to cracking of the material during hot compression-molding.

Ultimate recyclability has been shown in a practical way by re-molding used DMTA specimens into new test-specimens after pulverization of the initial sample by mechanical grinding. Recycling in this manner does not impart a significant detrimental effect on the thermoreversibility of the recycled material, as demonstrated by performing cyclic DMTA measurements where the obtained mechanical properties of the recycled PE-fur/Bism material were retained during these consequent cycles.

The excellent conservation of the tested properties of both virgin as well as recycled polymeric material during multiple thermal cycles indicates an already excellent recyclability. The additional re-processing of used material without any real loss of mechanical properties proves it is possible to fully recycle the described polyester/bismaleimide polymer using Diels-Alder chemistry.

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Chapter 4

Enhancing the impact properties of two Diels-Alder functionalized polymers through blending

4.1 Abstract

In order to overcome the inherent brittleness and improve the toughness of a polyester resin capable of thermoreversible crosslinking through Diels-Alder chemistry, blends are made with varying amounts of furan-functionalised rubber. In this way, the rubber can actively participate, via the furan groups, to the network formation and in principle be covalently linked to the polyester. Blank formulations were also prepared using non-functionalised rubber as reference. Blends containing up to 5% of rubber were successfully obtained. Izod impact tests show that a significant increase in toughness is obtained for the furan functionalised rubber whereas no effect is observed when incorporating the non-functionalised rubber. This indicates that inter-polymer crosslinking occurs, and plays a vital role in determining the final product properties.

4.2 Introduction

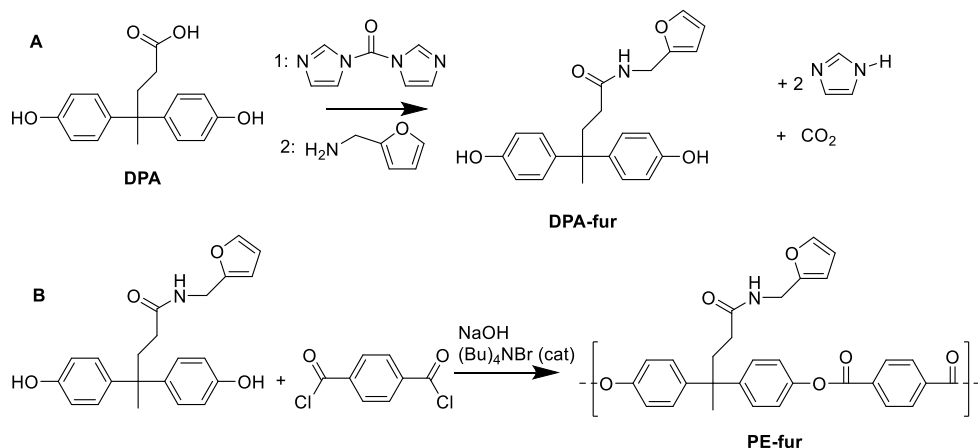
An increasing awareness regarding sustainability and the uncertain price development and availability of petroleum are encouraging academic and industrial research to develop new thermosetting resins from readily renewable carbon sources (i.e. bio-based)¹. In this context, 4,4-bis(4'-hydroxyphenyl)pentanoic acid, or diphenolic acid (DPA) has gained attention as a potential alternative to petroleum based bisphenol A (BPA), the key building block for epoxy resins and polycarbonates. DPA is a structural analogue to BPA, but may be considered to be fully renewable as it is synthesized by the condensation of levulinic acid and phenol². Levulinic acid is produced by the hydrolysis of biomass³, while phenol production from lignin-cellulose has also been described⁴. DPA and its ester derivatives, obtained by alkylation of the acidic group, have been used as diols to prepare thermosets such as high performance polybenzoxazines⁵ and epoxy resins⁶, exhibiting similar properties to the commercial ones, synthesized from BPA.

DPA based thermosets, as well as thermosetting resins in general, are (unfortunately) not designed to be recyclable according to a "cradle-to cradle" approach (i.e. by remoulding which is possible for thermoplastic materials). Thermosets and polyester based ones in particular are generally prepared via a liquid solution containing the various monomers to form a three-dimensional

covalently crosslinked structure¹. Once this reaction is complete, it is no longer possible to reshape the resulting material. Application of heat, sufficient to reshape most thermoplastic materials, would simply lead to degradation and decomposition of the thermoset. Therefore waste thermoset materials are currently reused as cheap reinforcement fillers or burned in order to recover (part of the) energy⁷. The application of reversible polymer networks represent a possible solution to this issue, since they combine the desirable mechanical properties of thermosets (high modulus, good solvent resistance, barrier properties) with the (re)processability and reworkability of thermoplastics⁸. The reversibility of these systems is based on the feasibility to break (part of) the crosslinks by applying an external stimulus (usually light or heat). The most studied covalent reversible systems are based on the Diels-Alder (DA) $[4\pi+2\pi]$ cycloaddition⁹ between a diene and dienophile moieties. In particular, the most investigated systems concern the furan/maleimide couple, mainly due to fast kinetics and high yields, as a consequence of the strong “diene” character (i.e. electron-rich) of the furan ring and the high reactivity of maleimide as a dienophile¹⁰. Notably, furan/maleimide adducts are formed at about 50 °C (crosslinking) while above 130 °C the equilibrium shifts towards the cleavage of the adducts (de-cross-linking via retro Diels Alder). Furthermore, the whole crosslinking/ de-crosslinking process can be repeated many times with negligible polymer degradation in the range of 50 °C – 150 °C¹¹.

A previous publication¹² describes the synthesis of a partly bio-based thermoset polyester from DPA, with the desired reversibility provided by Diels-Alder reactivity. The furan moiety was successfully attached to the DPA via amidation of the carboxylic group with furfurylamine (Scheme 1A). Next, the furan-modified DPA was reacted with terephthaloyl chloride, yielding a linear polyester (Scheme 1B) that could finally be crosslinked with aliphatic or aromatic bismaleimides. The resulting material displayed high recovery of mechanical properties during several heating-cooling cycles. Processability was improved by including phenol as a chain-stopper in the condensation step¹³, thus lowering the molecular weight and resulting glass-transition temperature (Tg) of the polyester.

Scheme 1: (A) Furan-modification of diphenolic acid DPA to DPA-fur and (B) polycondensation with terephthaloyl chloride

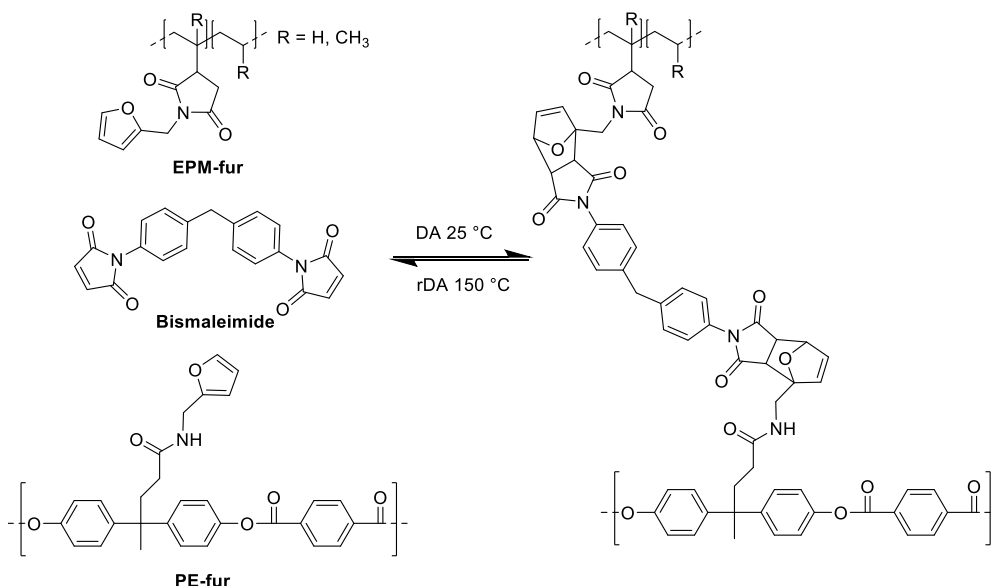


Thermosetting resins such as this one are inherently rigid and brittle. Rigidity and strength are required for many engineering applications, while brittleness or lack of crack growth resistance limits their application¹⁴. Elastomeric modification (e.g. rubber blending) is one of the most frequently used methods for improving toughness in thermosets¹⁵⁻²². Generally the applied rubber is required to have functional groups that are capable of reacting with the base thermoset resin²³ as can be observed in amine-terminated (ATBN) and carboxyl-terminated (CTBN) copolymers of butadiene and acrylonitrile, which are the most widely used toughening agents for epoxy resins^{24,25}.

Unfortunately, the application of these kind of conventional toughening agents would negate the thermoreversible crosslinking capabilities of the polyester/bismaleimide network mentioned above as these would react with the resin, effectively acting as a crosslinker. Unfortunately these crosslinks will be of an irreversible nature rendering the reversibility of the material moot. In a previous study it was shown that furan-functionalized rubbers can be used for the rubber toughening of thermoreversibly cross-linked thermosets with retention of recyclability²⁶. Therefore a furan functionalized EPM is suggested as toughening agent (Scheme 2). This chemically modified rubber has been proven, to be able to participate in thermoreversible crosslinking by use of the same DA reaction as homopolymer²⁷. It is to be expected that the furan functionality that is present in

both polymers (i.e. the EPM and the polyester) should allow for a fully reversible system based on Diels Alder chemistry in which both polymers are a part of the covalent network. The polyester imparts rigidity and the EPM acts as toughening agent, reducing the brittleness of the resulting material. This compatibility is expected to increase the miscibility and reduce the likelihood of phase separation.

Scheme 2: Crosslinking and de-crosslinking of furan-functionalized polyester PE-fur / EPM-fur rubber blends via Diels Alder (DA) and retro-Diels-Alder (r-DA) reaction with 1,1'-(methylenedi-4,1-phenylene)bismaleimide (b-Ma). The depicted reaction is expected to be the main contributor towards increased compatibility between the two components.



4.3 Experimental section

4.3.1 Materials

4,4'-Bis(hydroxyphenyl)valeric acid (DPA, Sigma-Aldrich, 95%), 2-methyltetrahydrofuran anhydrous (MeTHF, Sigma-Aldrich), N,N'-carbonyldiimidazole (CDI, Sigma-Aldrich, 97%) terephthaloyl chloride (Sigma-Aldrich, >99%), phenol (Sigma-Aldrich), tetra-n-butylammonium bromide (TBAB, Fluka), NaOH (Sigma-Aldrich, 97%), HCl (37%, Sigma-Aldrich), methanol (practical

grade, Interchema), chloroform (Lab-Scan), tetrahydrofuran (THF, Sigma-Aldrich, >99.9%) and 1,1'-(methylenedi-4,1-phenylene)bismaleimide (b-Ma) (Sigma-Aldrich, >95%) were purchased and used as received. Maleated ethylene/propylene rubber (EPM-MA, *Keltan 8550C*, 49 wt% ethylene, 49 wt% propylene, 2.1 wt% maleic anhydride, $M_n = 50$ kg/mol, PDI = 2.0) was kindly provided by ARLANXEO Netherlands. Furfurylamine (Sigma-Aldrich, >99%) was distilled prior to use. Deuterated dimethyl sulfoxide (DMSO- d_6 , Sigma Aldrich, ≥ 99.9 atom%) was used as solvent for ^1H NMR measurements.

4.3.2 Furan modification of diphenolic acid¹²

Diphenolic acid (5 g, 17.5 mmol), and *N,N'*-carbonyldiimidazole (1.2 equivalent, 3.40 g, 21.0 mmol) were weighed in a dry three-neck round bottomed flask connected to a cooler, under N_2 . MeTHF (30 mL) was added and the resulting mixture stirred under reflux conditions (90 °C) for two hours. Furfurylamine (1.2 equivalent, 1.85 ml, 21.0 mmol) was added and the reaction was allowed to proceed at 90 °C for an additional 5 h. The reaction mixture was then allowed to cool to room temperature and diluted with MeTHF (45 mL). The solution was washed with 1 M HCl (2 x 37 mL), 0.1 M NaOH (2 x 47 mL) and brine (1 x 15 mL) successively. Evaporation of the organic layer by rotary evaporation yielded a yellow oil. Final purification by recrystallization from ethanol yielded 3.26 g (51.1%) of a white solid (DPA-fur).

^1H -NMR (300 MHz, DMSO- d_6) δ 9.16 (s, 2H, OH) 8.19 (t, 1H, NH) 7.53 (s, 1H, fur-*p*) 6.93 (d, 4H, benzene-*o*) 6.62 (d, 4H, benzene-*m*) 6.35 (t, 1H, fur-*m*) 6.18 (d, 1H, fur-*o*) 4.19 (d, 2H, N- CH_2) 2.17 (t, 2H, - CH_2 -) 1.86 (t, 2H, - CH_2 -) 1.45 (s, 3H, - CH_3).

4.3.3 Polymerization of DPA-fur and terephthaloyl chloride¹³

The reaction of the DPA-fur monomer with terephthaloyl chloride results in a polyester containing pendant furan groups (PE-fur). The ratio of monomer/chain stopper added in this reaction was set at 4:2 to yield an average theoretical chain length of four monomeric repeating units, end-capped by two chain stoppers.

DPA-Fur (5.00 g, 13.7 mmol, 4 eq), TBAB (0.435 g, 8.7 %wt of DPA-Fur), phenol (0.644 g 6.84 mmol, 2 eq), NaOH (1.41 g, 34.2 mmol) and water (120 mL) were added to a 500 mL round bottomed flask. The mixture was stirred for 2 h at room temperature. Afterwards, terephthaloyl chloride (3.13 g, 15.4 mmol) dissolved in chloroform (120 mL) was added to the mixture. The reaction mixture was then

stirred overnight at room temperature. Precipitation in methanol (2 L) yielded a solid precipitate on the bottom of the beaker, as well as a suspension of small particles in the methanol phase. The methanol phase containing small solid particles was centrifuged in 50 mL cups at 4500 rpm for 15 min. Furthermore, the precipitate obtained in the centrifuge cups was filtered over a Büchner funnel and washed with water. Additionally, the solid precipitate on the bottom of the beaker was also filtered over a Büchner funnel and washed with water. Finally, all the solid products obtained were combined and dried in an oven at 70 °C for a 2 h to yield a white-yellowish solid (PE-fur, best yield achieved 74%).

¹H-NMR (300 MHz, DMSO-d₆): δ = 8.32-8.10 (m, 7H, aromatic not next to ester), 7.55 (s, 1H, fur-*p*), 7.49 (d, 1H, NH), 7.4-7.2 (m, 8H, aromatic next to ester), 6.37 (s, 1H, fur-*m*), 6.22 (s, 1H, fur-*o*), 4.23 (d, 2H, N-CH₂), 2.43 (s, 2H, -CH₂-), 1.98 (s, 2H, -CH₂-), 1.66 (s, 3H, -CH₃).

4.3.4 Furan-functionalization of EPM-MA rubber²⁷

EPM-MA was dried in a vacuum oven at 175 °C for one h to convert any diacid present into cyclic anhydride^{27,28}. Dried EPM-MA (100.0 g, 21.42 mmol MA) was dissolved in THF (≈ 10 wt % polymer) by stirring for 24 h at room temperature. Furfurylamine (6.24 g, 64.3 mmol) was slowly added to the solution. The reaction mixture was stirred in a closed system for 12 h at room temperature and then slowly poured into a tenfold amount of acetone (5 L). The polymer (EPM-fur), precipitated as yellowish flakes, was filtered and dried in an oven at 50 °C to constant weight. Amine conversion is determined by FT-IR on the basis of the decrease of the C=O asymmetric stretching band of anhydride rings at 1856 cm⁻¹ (using the methyl rocking bands at 723 cm⁻¹ as internal reference).

4.3.5 Sample preparation and crosslinking

Each blend was prepared by dissolving PE-fur and EPM-fur, combined at different weight ratios, in 100 mL THF at room temperature in a beaker. b-Ma was added in stoichiometric amounts (1:1 molar ratio between maleimide and furan groups of both polymers) and the reaction (Diels Alder cycloaddition) was allowed to proceed for 24 h at room temperature under agitation. Next, THF was partially removed by rotary evaporation (40 °C, 300 mbar). The obtained gel was dried in a vacuum oven at 50 °C for 24 h, ground and dried again in a vacuum oven at 140 °C for 1 h to yield a fine yellow powder. Reference samples, one containing PE-fur

and EPM-MA (95:5 wt% ratio) and another containing only PE-fur, were prepared and cross-linked with bismaleimide using the same procedure (Table 1). Samples have been coded by stating the type of EPM rubber and the weight ratio of rubber/polyester (in percentages).

<i>Sample</i>	<i>PE-fur</i> (g)	<i>EPM</i> (g)	<i>PE-fur/EPM</i> (w/w)	<i>b-Ma</i> (g)	<i>b-Ma</i> (mmol)
PE-fur*	10.00	-	100:0	2.68	7.50
PE-fur/EPM-fur_2.5	9.75	0.25	97.5:2.5	2.63	7.34
PE-fur/EPM-fur_5	9.50	0.50	95:5	2.57	7.18
PE-fur/EPM-MA_5*	9.50	0.50	95:5	2.55	7.13

Table 1. Amounts of PE-fur, EPM rubber (EPM-fur or EPM-MA) and b-MA used to prepare the samples and resulting wt% of rubber in each system *Reference samples

4.3.6 Characterization

¹H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz apparatus using DMSO-d₆ as solvent. FT-IR spectra were recorded using a Perkin-Elmer Spectrum 2000. Films (1 mm thick) were prepared from the EPM rubbers by compression molding at 180 °C for 30 min under a pressure of 100 bar.

DSC thermograms were recorded on a TA-Instrument DSC 2920 under N₂ atmosphere. Samples were first heated from 20 °C to 180 °C and then cooled to 20 °C. Four cycles were performed at a rate of 10 °C per min.

Dynamic Mechanical Thermal Analysis (DMTA) was performed using a Rheometric scientific solid analyzer (RSA II) under air, in dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 3 °C per min. Three cycles were performed for each specimen between room and softening temperature. DMTA specimens were on average 6 mm wide, 1.4 mm thick and 54 mm long. They were prepared by molding the cross-linked samples at 170 °C for 2 h under a pressure of 100 bar and then annealed in an oven at 50 °C for 24 h.

Izod impact strength was measured at room temperature, according to ASTM D4812 using standard unnotched specimens (12.7 mm wide, 3.3 mm thick and 64 mm long) prepared by compression molding of about 3.5 g of material at the same conditions as used for DMTA specimens and then annealed in an oven at 50 °C for 24 h. Tests were performed on a Zwick 5102 Pendulum Impact Tester equipped with a hammer. At least 10 specimens for each sample were tested. Impact strength was calculated as the ratio between the energy absorbed in the impact and the thickness of the specimen.

4.4 Results and discussion

4.4.1 Furan modification of EPM-MA

Furan-functionalized EPM rubber (EPM-fur) was obtained by reacting EPM-MA and furfurylamine in a THF solution at room temperature. The modification was studied by FT-IR transmission (see Figure 1). The most significant indication of the presence of furan groups is the appearance of the C-O-C symmetric stretching band at 1013 cm^{-1} ²⁹. Furthermore, the shift of the band at 1856 cm^{-1} to 1780 cm^{-1} (C=O asymmetric stretching) and the one from 1780 cm^{-1} to 1710 cm^{-1} (C=O stretching) in addition to the appearance of a new band at 1378 cm^{-1} (C-N symmetric stretching) confirmed the conversion of an anhydride into an imide^{28,30,31}. The areas under the peaks at 1856 cm^{-1} (C=O asymmetric stretching) and 723 cm^{-1} (methyl rocking vibration) were integrated by deconvolution analysis. From their ratio, the reaction conversion was found to be >99.9%, thus demonstrating that the chemical modification reaction is quantitative.

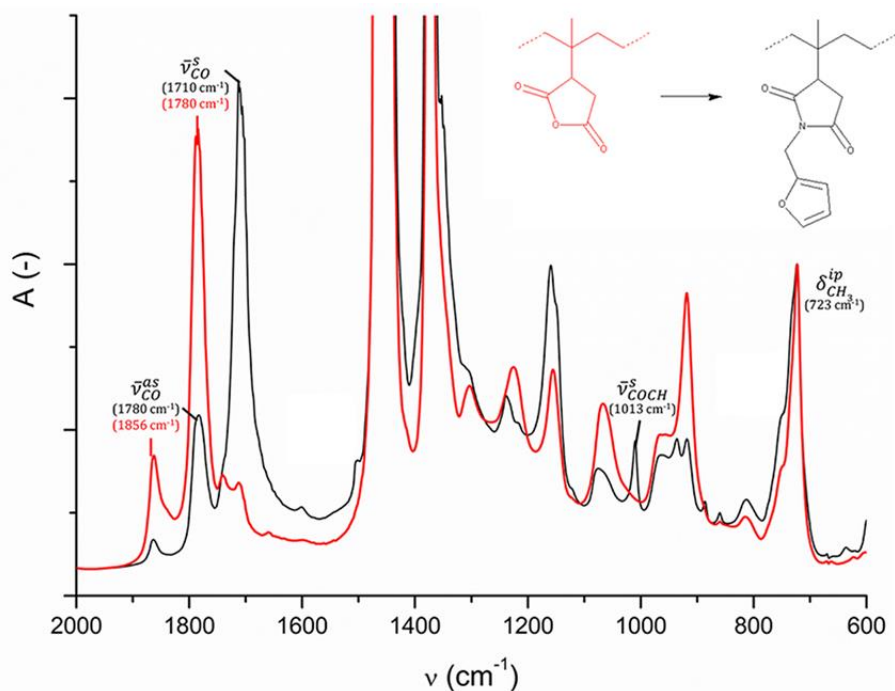


Figure 1: IR analysis of EPM rubber before (red) and after (black) functionalization with furan

4.4.2 Sample preparation and crosslinking

PE-fur/EPM-fur blends were combined and crosslinked in a THF solution at room temperature (Scheme 2, sample compositions reported in Table 1). The procedure reported^{12,13} previously for drying the pure polyester-bismaleimide networks (50 °C, 24 h in vacuum oven) did not yield sufficiently dry material when applied to the polyester/rubber blends. Coarse yellow particles were obtained which still contained a significant amount of solvent (evident from DSC). Therefore an additional drying step (140 °C, 1 h in vacuum oven) was required to achieve complete THF removal. Weighing the samples before and after drying showed the residual solvent content was about 10%. It seems that the solvent becomes trapped in the network, as it is only released once the *r*-DA temperature is reached. This finding is supported by DSC measurements where a large endothermic peak was observed around 140 °C.

A blend with an even higher polyester/rubber ratio (90:10) could not be prepared under these conditions, since the rubber precipitated in the form of millimeter-

scale sized particles, probably due to poor compatibility between the two polymers (i.e. the polyester is highly aromatic and polar, whereas the rubber is highly aliphatic and apolar).

All cross-linked samples were characterized by DSC in order to determine the thermal reversibility of the polyester/rubber/b-MA networks. In all thermograms, a broad endothermic transition in the range of temperature 130-180 °C, is observed for each consecutive thermal cycle (Figure 2). This transition corresponds with the retro-Diels-Alder (r-DA) reaction^{12,13,29,32,33}. The similarity in each consecutive thermal cycle demonstrates the reversible character of the crosslinked polyester alone or blended with the rubber.

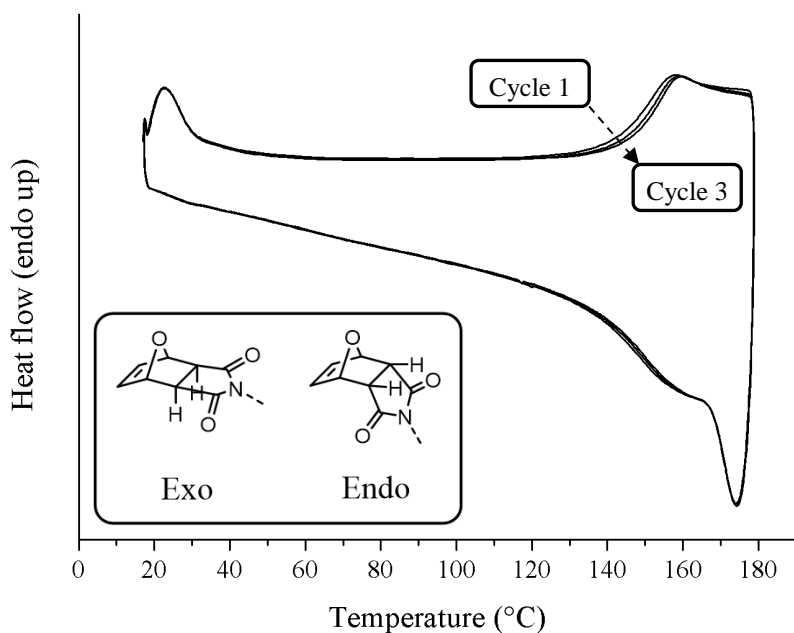


Figure 2: DSC thermal cycles of cross-linked PE-fur/EPM-fur_5 as representative example.

Inset: chemical structure of the exo and the endo stereoisomers of Diels Alder adducts.

When comparing the first with subsequent cycles, a slight shift (+ 2 °C) of the endothermic peak towards higher temperature was observed in all samples. This is consistent with previous observations reported for other thermoreversible networks based on the Diels Alder reaction with furan and maleimide^{9,34} as well as

for the b-MA crosslinked polyester^{12,13}. It may, thus, be attributed to the transition of DA adducts from the endo to the more stable exo conformation^{12,35}.

Ground samples were compression molded into homogeneous specimens (rectangular bars) suitable for DMTA (Figure 3).

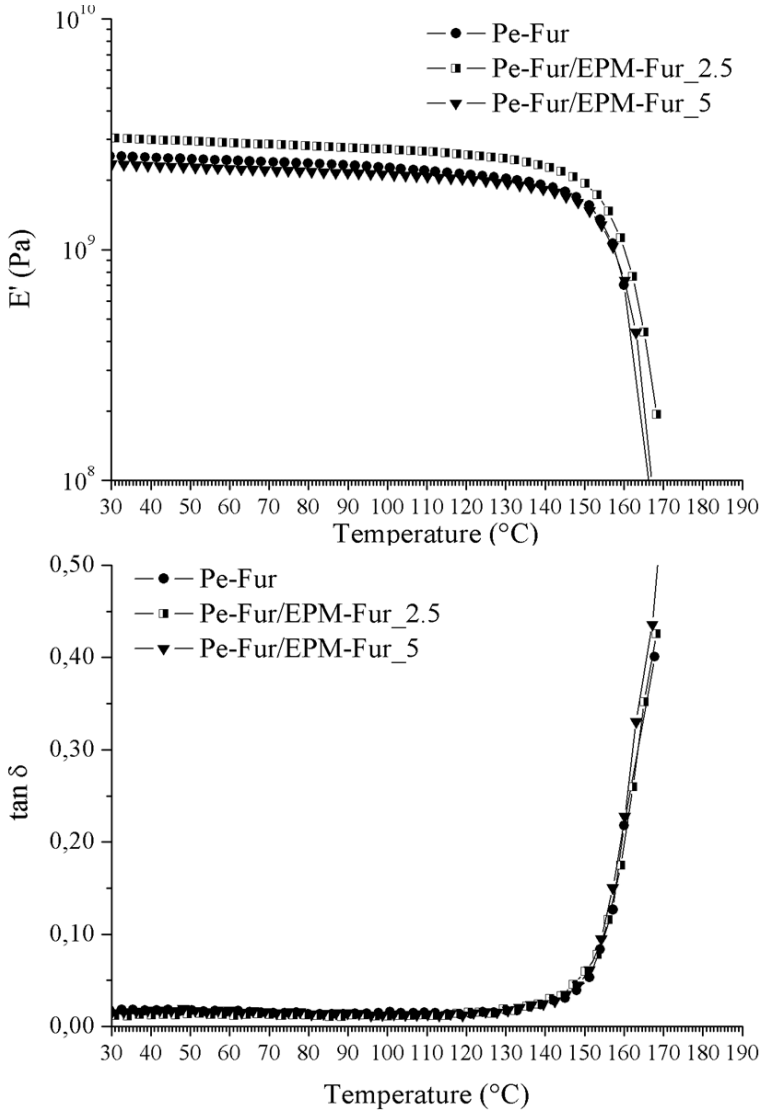


Figure 3: Storage modulus E' (top) and damping factor $\tan \delta$ (bottom) in DMTA during 1st heating stage for crosslinked PE-fur, PE-fur/EPM-fur_2.5 and PE-fur/EPM-fur_5.

For all samples the plateau in the storage modulus (E') that is characteristic for cross-linked polyesters was observed³⁶. This plateau is followed by a rapid drop at around 150 °C, implying a transition from elastic to viscous behavior. It appears that above this temperature the samples were still crosslinked, but softened due to partial cleavage of DA adducts¹⁰. Furthermore, the E' values in the plateau region appear not to be influenced by changes in the rubber content, suggesting that the rubber at these concentrations (up to 4 wt%) does not significantly affect the stiffness of the material. The softening temperature, as determined from the points of maximum decrease in E' , was found within a narrow range (168-171 °C) for all samples. After reaching the softening temperature, each sample was slowly (10 °C/min) cooled down to room temperature inside the DMTA chamber and tested again up to 3 heating cycles (Figure 4).

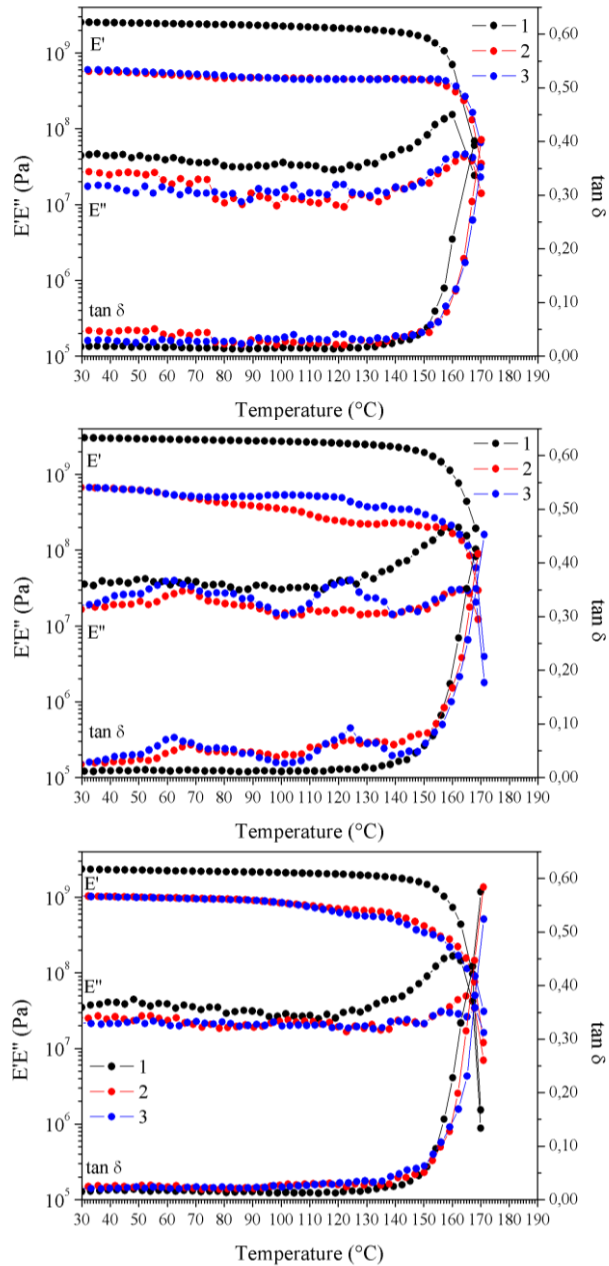


Figure 4: Storage modulus E' , loss modulus E'' and damping factor $\tan \delta$ of cross-linked samples PE-fur (top), PE-fur/EPM-fur_2.5 (middle) and PE-fur/EPM-fur_5 (bottom) for three consecutive DMTA cycles.

When comparing the first and second cycles, it is observed that storage moduli in the plateau region have slightly lower, but comparable values. This decrease was not observed when comparing the second and third cycles, suggesting that it might be due to deformation of the specimen at the end of the first heating stage. Indeed, when examining the samples after a measurement an elongation of several millimeters could be observed. This stems from the sideway force exerted on the sample by the DMTA sample holder. The slight increase in softening temperature (up to +2 °C) between subsequent cycles can be ascribed to the equilibrium between the kinetically favored *endo* and the thermodynamically more stable *exo* conformation of DA adducts^{12,37}. The constant stiffness of the material over consecutive heating cycles demonstrates the reworkability of the system, even in the presence of the rubber.

After performing thermo-mechanical tests on them, all specimens were re-ground and reshaped by compression molding (175 °C, 100 bar for 2 h) for another DMTA tests (Figure 5). In contrast to the freshly molded samples, the recycled materials exhibit lower but comparable storage and loss moduli and a slight (+1 °C) increase in the softening point, indicating full recyclability of the system. The return to similar mechanical properties after cooling down suggests that both polymers are able to re-form the DA crosslinks. Furthermore this hints towards the increased compatibility between both systems due to the shared crosslinking chemistry.

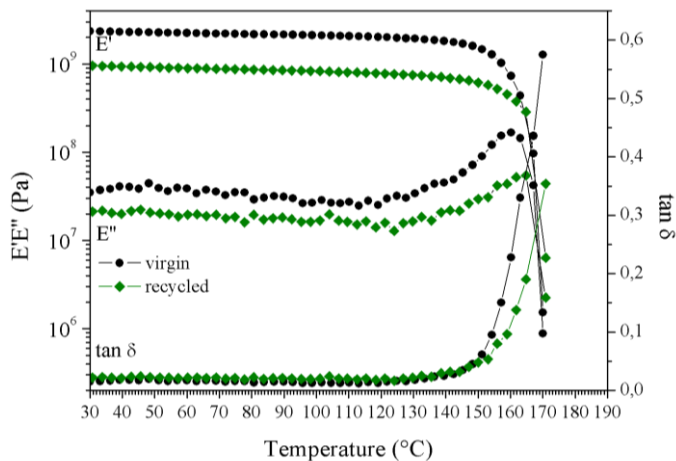


Figure 5: DMTA of cross-linked sample PE-fur/EPM-fur_5: comparison between virgin and recycled material. The recycled samples were reshaped at 170 °C and 100 bar for 2 hours

4.4.3 Impact strength

The Izod impact strength appears to monotonously increase with the amount of EPM-fur rubber (Figure 6). Ultimately, for the sample PE-fur/EPM-fur_5 (4 wt% of furan-modified rubber), a 54% increase in impact strength was observed compared to the neat crosslinked polyester. The two-tailed P value of an unpaired t test between PE-fur and PE-fur/EPM-fur_5 equals 0.0088, meaning this difference is “very statistically significant”. Meanwhile, no toughening effect was detected for the PE-fur/EPM-MA_5 (4 wt% of maleated rubber). This result indicates that, at least in this system, chemical bonding (i.e. Diels Alder cycloaddition) between the polyester matrix and the furan-modified rubber plays a crucial role in toughening, in agreement with what is generally reported for commercial rubber-toughened thermosets²³. Furthermore it serves as proof that the shared crosslinking capabilities of both polymers have successfully overcome the poor compatibility of the highly polar polyester and highly apolar EPM rubber.

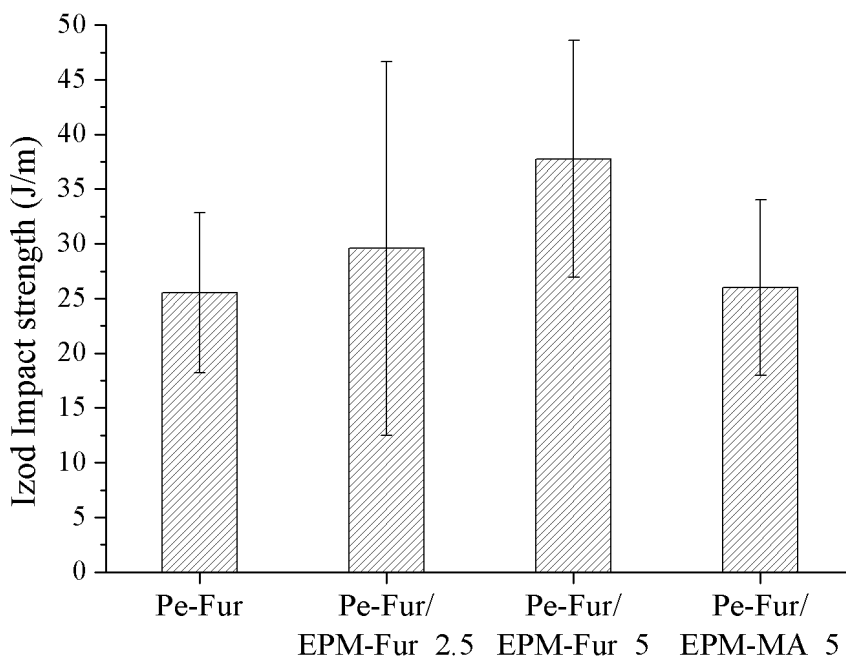


Figure 6: Izod impact strength of all b-MA samples Pe-Fur samples with and without different amounts of EPM-Fur. The error bars indicate ± 1 standard deviation.

4.5 Conclusion

Reversible, rubber toughened thermosets were prepared by mixing and cross-linking two different furan-functionalized polymers: a partially bio-based polyester, and an EPM rubber. The two polymers were successfully blended in different ratios (up to 5% in EPM) and crosslinked with an aromatic bismaleimide via the Diels Alder reaction.

Thermal reversibility was demonstrated by DSC for all prepared systems. Additionally, high recovery of mechanical properties was observed through cyclic DMTA measurements. Reworkability of the blends was demonstrated by remolding spent samples with little loss of mechanical properties.

The furan modified EPM rubber contributed to a significant enhancement (up to +54%) in toughness compared to the neat crosslinked polyester, as determined by Izod pendulum tests, without affecting mechanical properties, as determined by DMTA. While this improvement is to be expected for elastomeric modification of rigid thermosets, the fact that no significant effect was observed upon blending with non-functionalized EPM-MA indicates that the DA addition plays a crucial role. Furthermore it is a strong indication that covalent bonds are formed between both polymers, successfully overcoming the poor miscibility of the two.

4.6 Outlook

The preceding paragraphs make it abundantly clear that the toughness of a rigid polyester can be significantly improved by blending with an elastomeric component. It is clearly demonstrated that the shared capability of partaking in Diels-Alder crosslinking has a significant effect; in fact it seems required in order to see any improvement at all. The results imply an interaction between both polymers: allegedly Diels-Alder coupling occurs between the two systems. Unfortunately, no direct evidence could be obtained in order to prove this hypothesis. Therefore it would be beneficial to further analyze the system, focusing in particular on the cross-reaction between both components. Nevertheless, the results obtained are very promising and merit further investigation. A very straight-forward method of achieving greater control over the properties of the final blend would be the use of different rubbers. The

molecular weight and/or the backbone of the rubbers employed should provide ample possibilities of influencing the toughness of the final material.

4.7 References

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Chapter 5

The influence of amount and type of crosslinker on thermal and mechanical properties of a thermoreversibly crosslinked biobased polyester

5.1 Abstract

In an attempt to gain greater control over the product mechanical properties, a partially biobased, aromatic polyester capable of thermoreversible crosslinking via Diels-Alder chemistry is crosslinked using different types and amounts of crosslinker. The thermal and mechanical properties are analyzed by DSC and DMTA measurements, respectively. Three different bismaleimides were tested, all containing a different spacer, each in three different furan:maleimide ratios. Rather than the expected trend where lowering the crosslinker amount would lead to a reduction in the softening point a different behavior is observed where the softening point first increases and then decreases with decreasing amounts of crosslinker, displaying thus an optimum. This would imply that the ideal ratio of furans to maleimides in order to obtain the highest crosslinking degree (implied by the softening temperature) is not unity; rather a system starved in maleimides seems preferred.

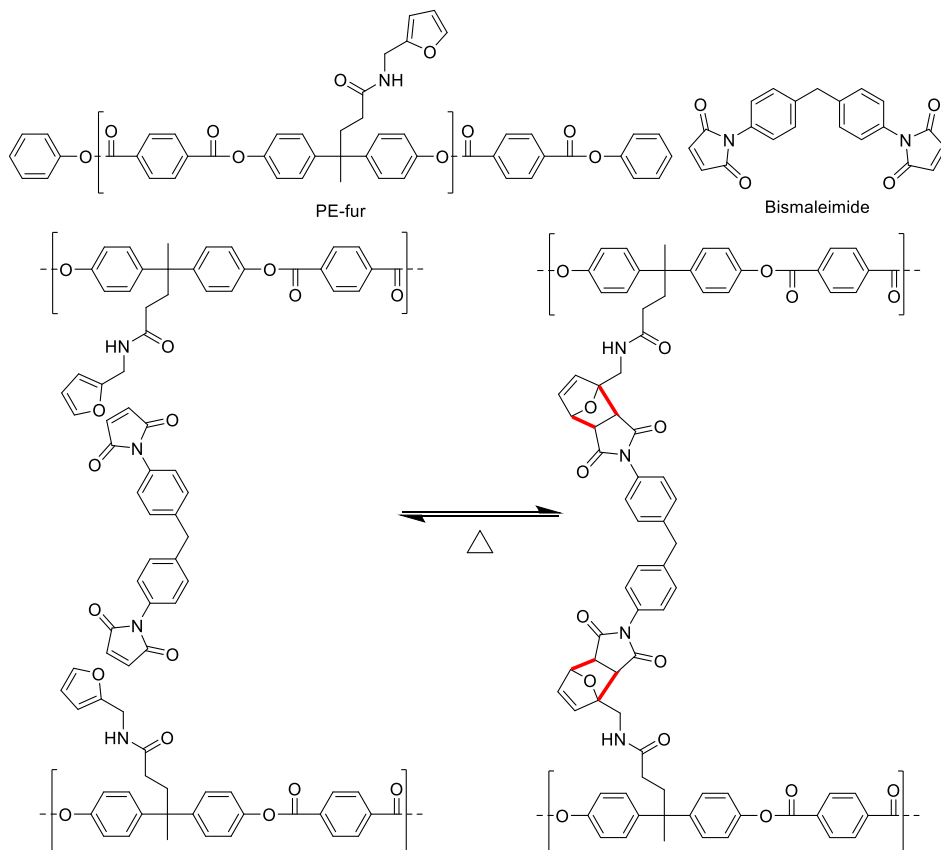
5.2 Introduction

The virtues of thermoreversible crosslinking of polymeric materials are well established by now¹⁻⁵, in particular the possibility for *cradle-to-cradle* recycling^{6,7}. In particular systems based on employing Diels-Alder chemistry have received much well-deserved attention⁸⁻¹¹: many publications describe its successful incorporation into various systems of vastly differing origin and properties and act as a testimony to its versatility and ease-of application. The Diels Alder reaction is a 2-component addition reaction between a diene and a dienophile, the furan (FUR) and maleimide (MAL) pair being often used for its convenient temperature range between the Diels-Alder coupling (DA) and retro Diels-Alder (rDA) decoupling reactions. In most cases a polymer is modified to contain only one of these two functionalities; in FUR/MAL systems usually the furan group is incorporated in the polymer. This approach ensures that the base polymer matrix does not undergo unwanted self-crosslinking reactions, making it easier to process. Crosslinking is initiated by the addition of a separate di- or multifunctional maleimide moiety. The reversible nature of this crosslink allows for superior properties of the material during application¹² (i.e. in the crosslinked state) while simultaneously enabling re-processability at elevated temperatures^{9,13} (i.e. in the decoupled state). However, this possibility does not

entail *per se* a solution to the underlying problem of depleting raw materials sources (i.e. oil) as, also in the case of *cradle-to-cradle* recyclable materials, dependence on petroleum resources might still be present, even if only to a lesser extent. To counteract this drawback, the use of biobased polymers might represent a convenient approach, provided that the possibility of recycling is retained. Previously, we described the synthesis of a highly aromatic and biobased furan-functionalized polyester¹⁴ which, after modification by a chain stopper, could be thermoreversibly crosslinked by addition of bismaleimide¹⁵ (see Scheme 1). This yields a thermoset-like material with excellent thermal reversibility, recyclability and re-processability. The application of a chain stopper allowed control over the properties of the uncrosslinked polymer by reducing its molecular weight and subsequently the T_g of the material before crosslinking. In the same work, the effect of the furan to maleimide ratio (in turn responsible for different crosslinking densities) was also explored. Indeed, a change in T_g of about 10°C was observed when halving the amount of crosslinker with respect to its stoichiometric amount. This preliminary result showed that the properties of the crosslinked material could be influenced as well by simple tuning of the intake of crosslinking agent. In order to achieve even greater control over the properties of the resulting material, this trend should be explored in greater detail. Besides the crosslinker intake, also the type of crosslinker (i.e. its chemical structure) employed can be used to influence the resulting material properties. Even though the chemistry of the systems remains mostly unaffected (i.e. the functional groups are still maleimides and furans), the use of different spacers between the two maleimide groups could also result in a relevant influence on the final material properties. This hypothesis is supported by a recent study investigating the effect of the spacer present in the bismaleimide crosslinker¹⁶ on mechanical properties of a thermally reversible rubber network. A significant effect in mechanical properties was observed when altering the furan to maleimide ratio. Furthermore a noted difference in crosslink density and resulting mechanical properties was observed when changing the crosslinker chemical structure, namely by altering the spacer between the maleimide groups. However, due to the fact that the base material used in this study is an elastomer, and the degree of functionalization (and therefore also the degree of crosslinking) is low even at the highest furan to maleimide ratio (typically in the order of 10^{-5} mol/gram), direct comparisons with

the highly functionalized polyester would be rather speculative. On the other hand, Zeng *et al*¹⁷ also report significant changes in material properties by altering

Scheme 1: Diels-Alder coupling between PE-fur and bismaleimide



the type and amount of crosslinker employed. Indeed, for the polymer employed (a polyester of bis(hydroxymethyl)furan and succinic acid) a change in softening temperature of about 5 degrees is observed when changing the type of crosslinker spacer from $-(\text{CH}_2)_6-$ to $-(\text{C}_6\text{H}_4)-$. Interestingly, the effect of the type of spacer on T_g differs for each ratio (see Figure 1): at FUR:MAL ratio 2:1 the $-(\text{CH}_2)_6-$ spacer displays the highest T_g , and the $-(\text{C}_6\text{H}_4)-$ spacer the lowest, while at FUR:MAL ratio 6:1 the T_g of the $-(\text{CH}_2)_6-$ is actually lower than that of the $-(\text{C}_6\text{H}_4)-$, furthermore the spacers giving both the highest and lowest T_g at this ratio display identical T_g at FUR:MAL ratio 2:1. This clearly demonstrates that various factors, often in a synergic manner, display a relevant influence on the final properties of

the material. The main properties of the spacer are its rigidity and length: a longer and/or more flexible spacer should yield a less rigid material. This should be visible in the moduli of the crosslinked material. However, another influencing factor is the miscibility of the compounds: when the crosslinker is poorly miscible with the polymer matrix, its mobility throughout the material will be limited leading to less effective crosslinks. This can lead to lower softening temperatures, differing moduli or, in extreme cases, an inability to form a homogeneously crosslinked material altogether.

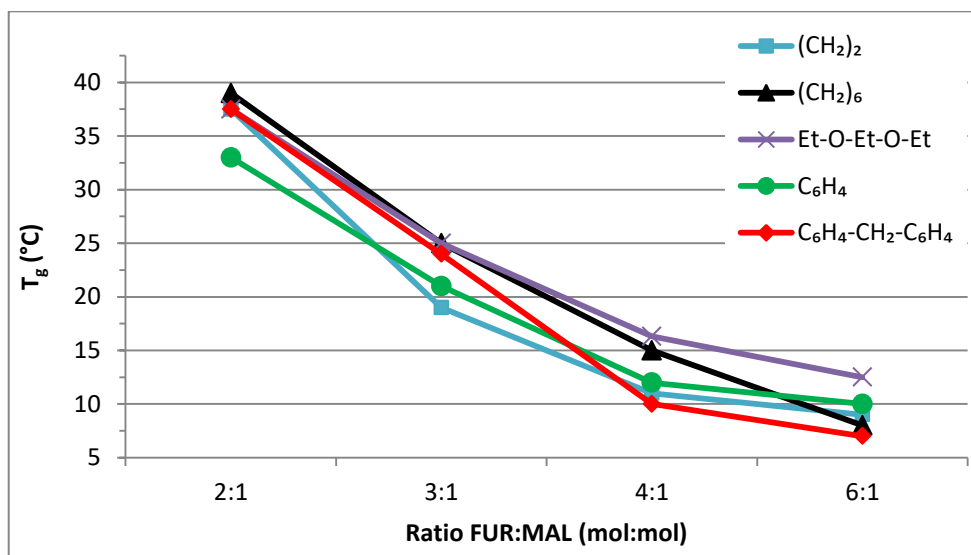


Figure 1: softening temperatures of poly-bis(hydroxymethyl)furan/succinic acid networks containing different crosslinker spacers in different ratios

The aim of this work is determine the effect of systematically changing both the furane to maleimide ratio and the spacer present in the bismaleimide on thermal and mechanical properties of the resulting polymer network. In order to assess this, mixtures consisting of the aforementioned polymer (PE-fur, see Scheme 1) and various amounts of different bismaleimides have been prepared and analyzed. Aromatic and aliphatic bismaleimides are used to elucidate the effect of miscibility with the highly aromatic base-polymer on mechanical properties.

5.3 Experimental section

5.3.1 Materials and equipment:

THF and *N,N'*-(1,4-Phenylene)dimaldimide were obtained from Sigma-Aldrich and used as received. *N,N'*- hexamethylene dimaleimide and *N,N'*- octamethylene dimaleimide were prepared according to the procedure described in literature¹⁴. PE-fur was synthesized according to the procedure described previously¹⁵.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer differential scanning calorimeter Pyris 1 under N₂ atmosphere. Before DSC's the sample was weighed (ca. 12 mg) and subsequently heated from 25 °C to 180 °C. Multiple cycles were performed at a heating rate of 10°C/min throughout the measurements. DMTA measurements were performed using a Rheometrics scientific solid analyzer (RSA II) under air using dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 5 °C/min.

5.3.2 Preparation:

All samples were prepared according to the following procedure:

A round bottom flask was charged with 5 gram polymer (PE-fur) and 50 ml THF. The mixture was stirred at ambient temperature until all the polymer had dissolved, after which the required amount of crosslinker was added (e.g. 1.04 grams for the C6 1:1 sample) while still stirring. When a clear solution was obtained, most of the THF was removed by airflow at ambient temperatures, the resulting gel was dried in a vacuum oven for 4 hours at 50°C yielding a yellow solid. As previously established THF removal is incomplete while following this procedure¹⁸ so subsequently this solid was frozen with liquid nitrogen, ground to fine particles using an Ika industrial grinder and placed in the vacuum oven once more at 140°C overnight. This gives the final material in quantitative yields. A summary of all formulations prepared is given in Table 1

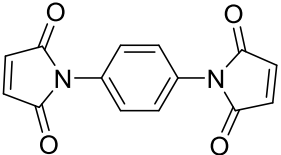
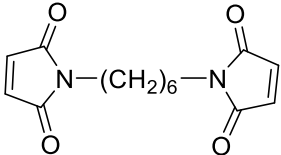
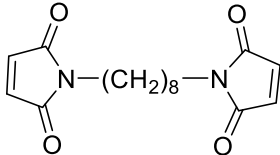
								
Benz 1:1	Benz 2:1	Benz 4:1	C6 1:1	C6 2:1	C6 4:1	C8 1:1	C8 2:1	C8 4:1

Table 1: Overview of all formulations tested in this work, samples are identified by spacer group and FUR:MAL ratio (mol:mol)

5.3.3 Analysis

In order to obtain the rDA enthalpy, DSC results were interpreted as follows: first a straight baseline was defined. This was done by choosing the outer limits of the peak in such a way that a straight line between these points gave the largest peak area without crossing the graph (see Figure 2 for an example). This baseline was then subtracted from the graph, after which the local maximum was determined which was defined as the softening temperature. Finally the integral of the obtained peak was obtained (Table 2 and Figure 5).

DMTA samples were prepared by placing approx. 0.5 grams of material in a mold, which is placed in a press and heated to 180°C before applying 100 bars of pressure to it for 30 minutes. Afterwards the sample was allowed to slowly cool to ambient temperature inside the press. The softening point obtained via this measurement is defined at the initial point of decrease of the modulus.

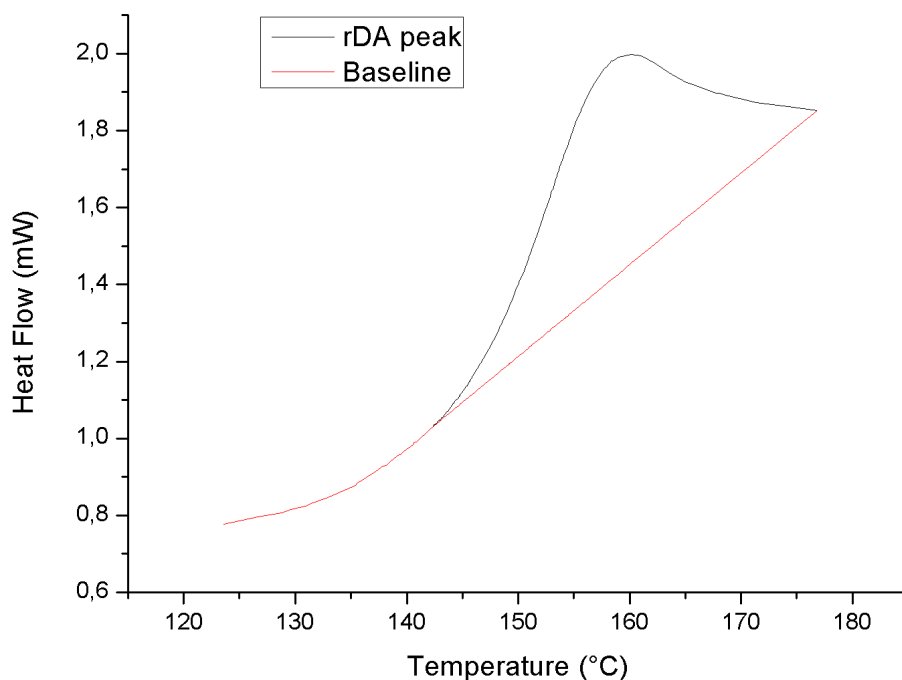


Figure 2: Example of baseline definition

5.4 Results and discussion

Using the procedure described 9 compounds were successfully synthesized, each containing one of three different crosslinkers and one of three different ratios of maleimide to furan groups present (see Table 1). The difference between the crosslinkers lies in the chemical composition of the spacer. As the procedure consisted of blending followed by solvent removal all yields are stoichiometric. IR analysis of the formulations in order to assess the degree of crosslinking proved impossible due to peak overlap with background signal. Therefore analysis was based on the thermal and mechanical properties. First the thermal behavior of all prepared samples was analyzed by DSC (see experimental part) on consecutive heating/cooling cycles from ambient temperature to 180°C (Figure 3).

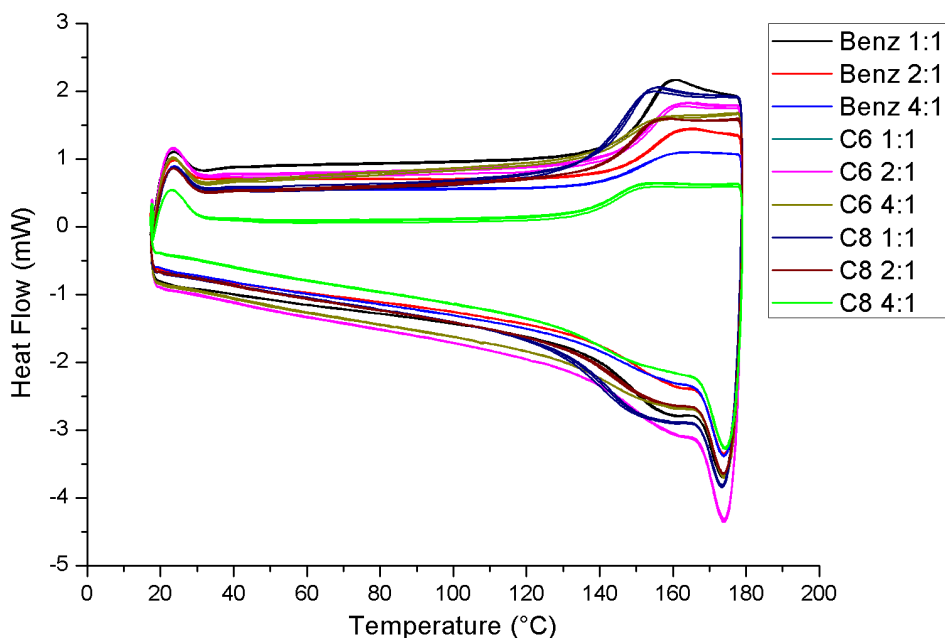


Figure 3: Cyclical DSC measurements for all prepared samples

The first observation that can be made is the overlap of all cycles (i.e. comparing thermograms of the same sample upon different heating/cooling cycles): this means that the thermal properties do not change over the course of heating and cooling. The next observation is that all samples display a peak around 150°C. This peak is attributed to the rDA reaction¹⁴. The fact that these peaks are present in each heating step indicates that all samples undergo the rDA reaction during heating. The corresponding peaks in the cooling steps also confirm the (re)occurring of Diels Alder upon cooling. It is worthwhile to stress that the rDA peak shifts depending on the kind and amount of crosslinker. In order to elucidate this more clearly (Figure 4), further analysis was carried out.

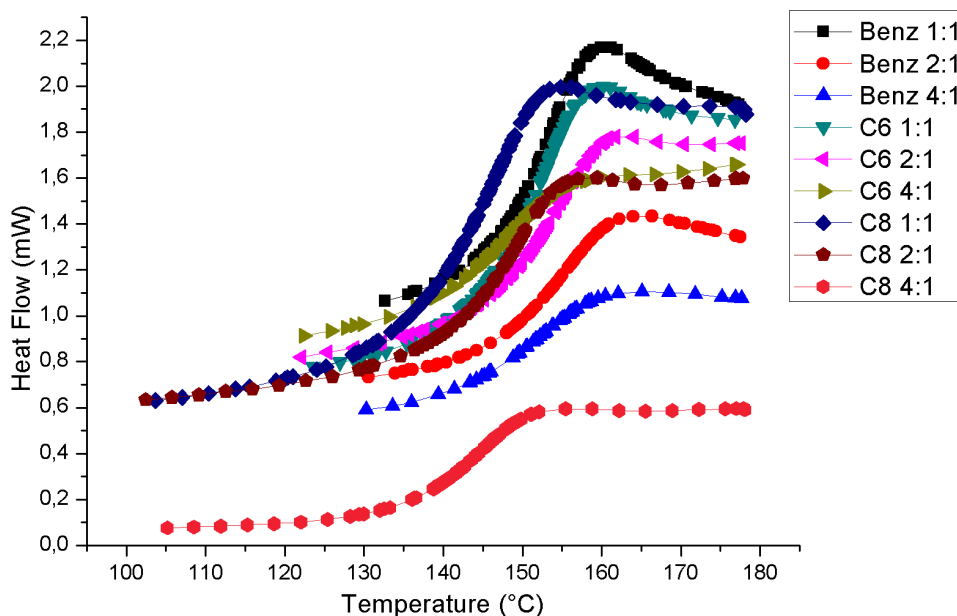


Figure 4: DSC 2nd heating cycles of all materials.

The exact rDA temperature and enthalpies of all samples were determined (see experimental part for the procedure) and are summarized in Table 2 and Figure 5. As the value obtained directly from DSC corresponds to the enthalpy per gram, a normalization was applied to obtain the enthalpy per mole bismaleimide present.

Crosslinker	Benz			C ₆			C ₈			
	FUR:MAL Ratio (mol:mol)	1:1	2:1	4:1	1:1	2:1	4:1	1:1	2:1	4:1
Temperature (°C)		159	162	159	158	160	156	152	155	152
ΔH_{rDA} per gram		9.9	5.0	3.8	9.1	5.8	5.0	12.6	7.0	5.0
ΔH_{rDA} per mole bismaleimide		15.9	14.7	21.3	14.6	17.1	28.0	20.6	20.8	28.2

Table 2: Softening temperatures and enthalpies from DSC

On initial inspection it appears that the rDA enthalpies follow the expected trend where halving the amount of crosslinker present leads to halving (roughly and within the experimental error of the measurement) of the area of the rDA peak. This behavior is expected as the area of the rDA peak is correlated to the extent of

the rDA reaction. Sample C6 4:1 breaks this trend, but this is likely due to the analysis method: the proximity of the endotherm to the baseline result in higher relative error for the area.

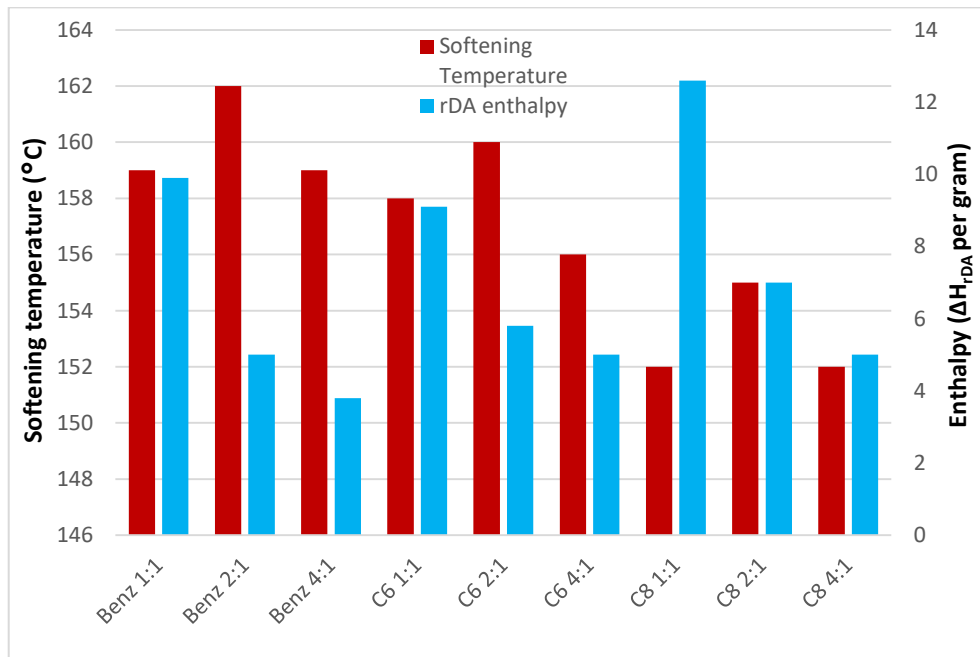


Figure 5: Softening temperature and rDA enthalpy for all samples

Interestingly, it appears that both the type of spacer as well as the ratio of maleimides to furans have an effect on the rDA temperature. As far as the ratios are concerned, a trend is observed where the samples with ratio 1:1 and 1:4 have a comparable rDA temperature while for the sample with a ratio of 1:2 this shifts to several degrees higher. It would seem that the network formed plays a role in the rDA temperature: at the 1:1 FUR:MAL ratio the sample seems to be oversaturated, meaning that many bismaleimides are only bound with a single maleimide group. Once this single maleimide undergoes rDA decoupling it is no longer part of the network, and can move around freely. The 1:2 FUR:MAL samples likely consist of a (tight) network where most, if not all, bismaleimides are bound with both maleimide groups, when the first maleimide group undergoes rDA decoupling, it is kept in place by the remaining polymer matrix, which still consists of highly crosslinked material. This lack of mobility increases

the local concentration of maleimide and furans leading to a more stable DA adduct. In the case of the 1:4 FUR:MAL ratio it seems that the residual polymer matrix obtained after breaking the first DA couple is not rigid enough to hamper the mobility and the resulting softening temperature is similar to the 1:1 ratio. This explanation is supported by the normalized enthalpy values: the enthalpy per mole of bismaleimide increases significantly over the range of ratios examined with the 1:4 samples yielding the highest values. This value represents the energy consumed per mole of bismaleimide present, which means it can serve as an indication of crosslinking effectiveness: a lower value would indicate that on average more maleimide groups are not participating in Diels-Alder coupling (*e.g.* do not require energy to decouple). The samples with the lowest amount of bismaleimide present (1:4) display the highest rDA enthalpy per mole, which is therefore indicative of the highest degree of DA coupling. The fact that the 1:2 sample displays a lower normalized enthalpy (*i.e.* enthalpy per mole) indicates that not each maleimide present is participating in DA adduct formation, leading to singular adducts of bismaleimide. These singularly bound bismaleimides will undergo rDA decoupling first leaving a rigid polymer network (*vide supra*). Finally, the 1:1 sample displays an even lower normalized enthalpy, which in turn implies that most bismaleimide molecules are only bound via DA adducts with a single maleimide group. There is no rigid network keeping these bismaleimides in place hence the softening temperature is lower.

It seems that the type of spacer also has an effect on the rDA temperature. This is somewhat surprising as the spacer is unable to participate in the reaction, *i.e.* the coupling occurs between the furan and maleimide, which are the same for all spacers. When comparing the spacers for each ratio, a trend is observed where the rDA temperature decreases steadily from benz to C6 with C8 giving the lowest values (Figure 6). A possible explanation for this behavior can be found in the compatibility of polymer matrix and crosslinker (bismaleimide). One would assume that due to the polymer being highly aromatic and the crosslinker quite aliphatic the miscibility of C6 and C8 in particular is quite poor. However, when looking at the solubility parameters of all chemicals (Table 3) it becomes clear that the C8 crosslinker is most miscible with the polymer due to the similarity of their solubility parameter (δ). Furthermore the high miscibility of the C8 spacer combined with the lowered rDA temperature suggests that decoupled maleimide

is free to move about the polymer driving the reaction to the decoupled products at lower temperature.

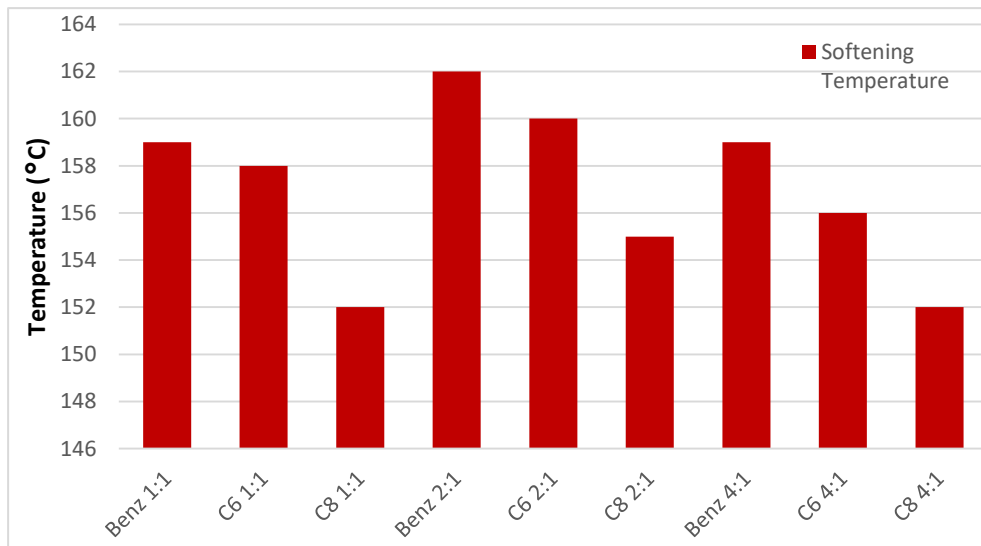


Figure 6: softening temperatures grouped per FUR:MAL ratio

This in turn suggests that the poor miscibility of the C8 and aromatic spacers are responsible for the higher rDA temperatures, and the more stable adduct.

	Solubility parameter (J/cm ³) ²		Solubility parameter (J/cm ³) ²
Polyester	11.4		12.6
	15.1		11.9

Table 3: solubility parameters of all chemicals involved¹⁹

5.5 Mechanical analysis (DMTA)

In order to gain further insight into the behavior of all samples, mechanical properties were determined by DMTA as well (Figure 7). Unfortunately it turned out to be impossible to isolate the pressed bars of sample benz 4:1 as these

turned out too brittle to remove from the mold intact, possibly due to the poor miscibility of the polymer and crosslinker. The first heating steps of all DMTA measurements are depicted in Figure 7. Upon closer inspection an interesting observation can be made: all samples (sample Benz 1:1 being a slight outlier) display basically the same modulus. Considering that identical moduli indicate identical crosslinking degrees²⁰, this observation supports the hypothesis that the 1:1 samples are oversaturated. However, the 2:1 and 4:1 samples displaying the same modulus, challenges this statement as this would indicate that also the 2:1 samples are oversaturated or are otherwise forming inefficient crosslinks. However, as these measurements are performed on the bulk of the material, their nature makes it impossible to draw conclusions on a molecular level. While the first bond breakage can be detected with DSC as the start of a peak, DMTA only gives an outcome when enough bonds have broken to have a significant influence on the material properties.

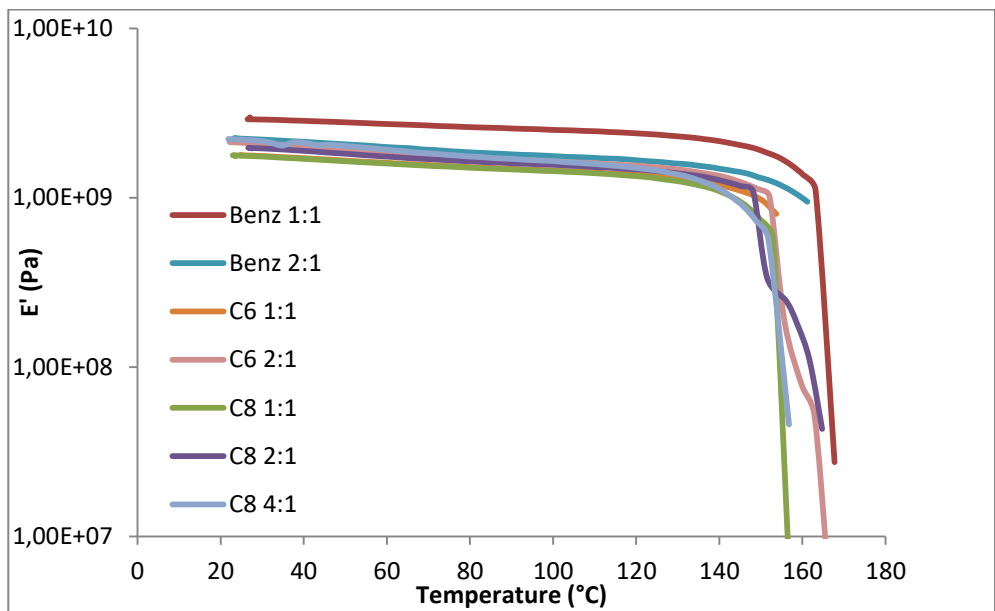


Figure 7: DMTA results of all samples measured, only E' values for the first cycles are shown

The softening temperature has been determined from these DMTA results. It is defined as the steep decrease in modulus which occurs around 150°C. The values obtained thusly are given in Table 4.

	Softening point (°C)		Softening point (°C)		Softening point (°C)
Benz 1:1	160	C6 1:1	154	C8 1:1	153
Benz 2:1	161	C6 2:1	152	C8 2:1	148
				C8 4:1	152

Table 4: softening points obtained from DMTA results

The first thing to notice is the fact that some samples (C6 2:1 and C8 2:1 in particular) display a two-step softening. This further supports the hypothesis that the resulting polymer matrix is able to support DA formation by keeping both groups in close proximity. A possible explanation for this phenomenon could be that the first step corresponds to the opening of only part of the bonds, leaving a material which still possesses a relatively strong network, and thus a relatively high modulus. When the softening temperatures are compared to the DSC results the trend where the 2:1 samples display a softening temperature several degrees higher seems no longer present due to their two-step softening profile. However, if the softening point is defined differently, namely as the final point measurable, the trend persists.

After the first heating cycle all samples were cooled while still in the device and measured again, these cycles were repeated twice more. Looking from the 2nd heating cycles onwards some differences begin to appear: the moduli of different ratios start to diverge, however as they become more erratic comparing the samples becomes difficult. For the aromatic spacer a small decrease in modulus is observed by halving the amount of crosslinker present. As the second cycle constitutes the re-crosslinked material it makes sense that the sample with more crosslinker present is able to form a material with a higher modulus and thus a higher crosslinking density. The material displays a consistent softening point for all heating cycles, indicating thermoreversible crosslinking capabilities with no side reactions. For the C6 spacer, the data for the second cycle onwards is even more erratic and the modulus fluctuates greatly during the measurement. As stated, these measurements are on recrosslinked materials. Therefore it is likely that the poor miscibility of polymer and crosslinker hamper the formation of a crosslinked network. The 2:1 sample, for instance, displays the lowest modulus of all samples measured (below 10^8 pa) indicating the lowest crosslinking degree. And while the 4:1 sample initially maintains the same modulus as the 1:1 sample,

in the final measurement the modulus also drops below 10^8 pa. Finally, the C8 spacer displays the trend observed in DSC where once again the 2:1 sample displays a lower modulus, and both 1:1 and 4:1 samples give very similar results.

When comparing the results obtained with previous findings²¹ some interesting conclusions can be drawn. Firstly, using the same polymer and a dibenzyllic bismaleimide softening points of 146°C and 136°C were reported for 1:1 and 1:2 ratios respectively, as determined by DMTA. These values are significantly lower than all the values obtained with the three crosslinkers described here. Furthermore, the softening points adhere to the “classical” explanation where the value obtained for the 2:1 is lower than that of the 1:1 by a significant amount (10°C). The solubility parameter (δ) of this spacer is $13.5 \text{ (J/cm}^3)^{1/2}$, which is between the aromatic and C6 spacers. There are two possible explanations: firstly the dibenzyllic crosslinker is capable of participating in π - π interactions with the (highly aromatic) polymer by virtue of its two benzene rings. This interaction could be beneficial, giving the two components better compatibility ultimately leading to better miscibility despite the large difference in solubility parameters. As seen for the C8 spacer, good miscibility lowers the rDA temperature. Secondly, however, is the fact that since these are DMTA values the size of the crosslinker also plays an important role: in DSC only the thermal properties are observed. This means that a (longer) spacer between two groups only has an effect on miscibility, the strength of the resulting material is not taken into account. In a DMTA measurement however, the strength of the resulting material is measured, and a longer spacer is expected to give a wider, more flexible (i.e. less densely crosslinked) network. This should result in a lowering of the modulus as well as the softening temperature as the material is already relatively mobile even in its crosslinked state.

5.6 Conclusions

The PE-fur polyester has successfully been crosslinked using bismaleimides in various ratios of maleimide to furans and containing different bismaleimide spacers. The resulting products display successful thermoreversibility in both DSC and DMTA analyses. Both thermal and mechanical properties show little change over the course of consecutive heating/cooling cycles. The rDA- or softening temperatures obtained for the three crosslinkers follow a trend that corresponds to their miscibility with the polymer: the benz spacer, having the poorest miscibility due to a significantly different solubility parameter, displays the highest rDa temperature. Next is the C6 spacer, having a better miscibility and a comparable solubility parameter and finally, the C8 spacer having a nearly identical solubility parameter displays the lowest rDA temperature. As the Diels-Alder reaction is an equilibrium reaction it is within expectations that a poor compatibility of chemicals leads to a shift away from this mixture (i.e. an increase in rDA temperature which would yield the decoupled products). The DSC integrals (which represent the rDA enthalpies) on first inspection would suggest that most of the maleimide groups are participating in DA additions as halving the amount of maleimide roughly halves the integral. However upon normalizing the values for the amount of bismaleimide present, it appears that samples 1:1 and 1:2 are oversaturated in bismaleimide as the rDA enthalpy per mole is significantly lower compared to the 1:4. Furthermore from DMTA data it appears a significant amount of bismaleimide molecules do not participate in effective crosslinking as the moduli of samples containing a 1:1 FUR:MAL ratio are nearly identical to samples containing a 2:1 ratio. If all maleimides partake in effective crosslinking, a more rigid material should be formed for the 1:1 ratio as this should be more densely crosslinked. Consequently a significant effect would be observed when halving the amount of bismaleimide.

5.7 References

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Chapter 6

Closing the chain: a technological assessment

6.1 Introduction

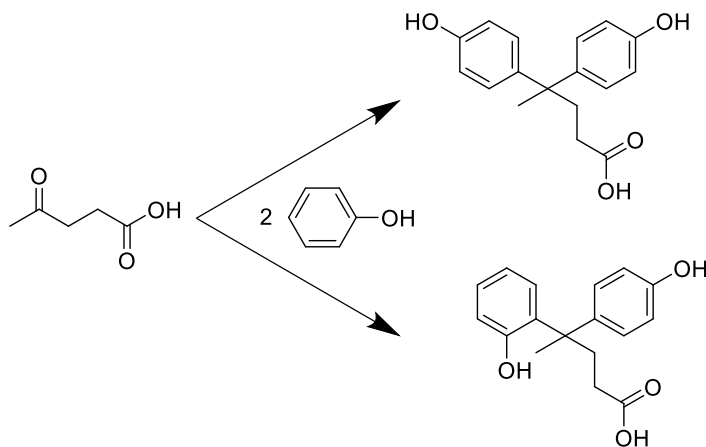
Throughout this thesis a route has been laid out for the synthesis of a biobased, reversible thermoset-like material able to be reprocessed and reworked like a thermoplastic. Various steps have already been taken successfully: the functionalization of DPA, its subsequent copolymerization and successful thermoreversible crosslinking. However, other important steps must be taken when making allowances for the full chain, i.e. from biomass to final product. This assessment will address two parts: the first part will, deal with the first reaction in the whole process: the synthesis of diphenolic acid itself from levulinic acid and phenol. While both of these starting materials are obtainable from renewable resources, the currently employed process which combines them could be greatly improved from a sustainability viewpoint as the current commercial process consists of homogeneous catalysis in the form of dissolved Brønsted acids¹⁻³. The application of a heterogeneous catalyst would hold various obvious benefits such as facile catalyst removal and recovery.

The second part of this assessment will discuss the application of the thermoreversible material in a real-life application. In their pure form, the polymers described in this thesis show excellent reworkability, reprocessability and recyclability. However these materials are rarely used in their pure form. In order to either reduce costs or improve the mechanical properties of the final product, thermosets are often blended with fibrous materials. To test the viability of this material, blends were prepared with fibrous materials. In line with the philosophy of this work, only fibers obtained from renewable resources were employed.

6.2 Part 1: DPA synthesis using heterogeneous catalysis

The currently employed process for the synthesis of diphenolic acid from levulinic acid utilizes dissolved Brønsted acids. The implementation of a heterogeneous catalyst holds many potential merits such as catalyst reusability. Fortunately, these merits have been recognized and previous publications describe the synthesis and application of various heterogeneous catalysts for the synthesis of diphenolic acid. Furthermore there are significantly more catalysts described for the (very similar) synthesis of bisphenol A, providing an even larger knowledgebase. All reported catalysts are rated based on three aspects: activity, selectivity and stability. The selectivity of the reaction is negatively affected by the formation of an unwanted isomer during the reaction. This isomer is obtained due to the fact that phenol can react with levulinic acid in two positions of the phenolic ring: ortho and para (Scheme 1). The *o,p*-isomer is unwanted as the *p*-OH group is unavailable for further reactions due to steric hindrance. Stability is not often addressed in detail, however some publications^{4-6,6} mention the possibility of repeat experiments after a catalyst regeneration step.

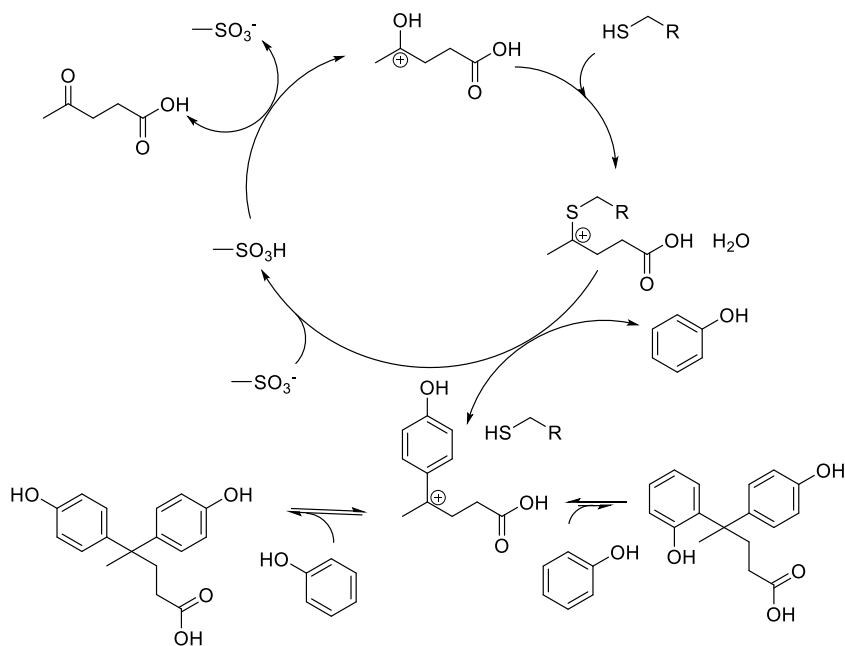
Scheme 1: *o,o*-isomer (top) and *o,p*-isomer (bottom) of DPA condensation reaction



It is widely accepted that the synthesis of DPA benefits from strong Brønsted acidity and, although not fully understood, that the presence of thiols in the reaction mixture has a favorable effect on the ensuing selectivity. Various mechanisms have been proposed about the exact role of the thiol, mostly assuming its role to be mostly based on steric hindrance driving the selectivity.

However van de Vyver *et al.* report⁷ significantly reduced activity and selectivity when changing the cocatalyst from ethanethiol to 1,1-dimethylethanethiol under otherwise identical conditions. This has led them to propose the mechanism depicted in Scheme 2.

Scheme 2: proposed mechanism for DPA synthesis involving thiols as cocatalyst



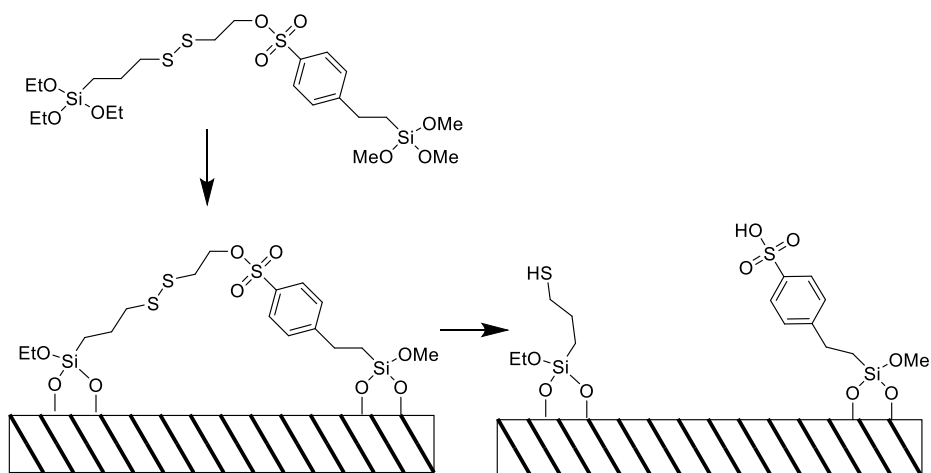
Various systems have been described as potential candidates for the role of heterogeneous catalyst: sulfonation of carbon, giving strong Brønsted acidity on a heterogeneous carrier⁸; zeolite materials^{1,9}; immobilization of bifunctional precursor resulting in a proximity effect of thiol and acidic group¹⁰; immobilized heteropolyacids on Cesium^{6,11}, silica⁵ or clay¹², etc. ...

The use of a sulfonic acid group immobilized on carbon is a very straightforward implementation of strong Brønsted acidity and can easily be complemented with thiol functionalities as well, which should greatly enhance selectivity and activity. Unfortunately the material suffers from leaching of the acid group, significantly reducing its activity over the course of multiple cycles. The immobilization of a bifunctional precursor onto silica is a very elegant concept based on the assumption that proximity of thiol and Brønsted acid groups promotes the

selectivity of the reaction even further. The procedure is depicted in Scheme 3. Unfortunately, despite the elaborate synthesis, the authors report only a relatively small effect on selectivity¹³.

Finally, heteropolyacids (HPAs) hold great promise as these have been used with great success in the synthesis of bisphenol A^{11,14}. Furthermore, a positive effect on yield and selectivity was observed upon implementation of diethylaminothiol (DEAT) as co-catalyst⁷. Some results have already been reported using immobilized HPAs of both Keggin ($H_3PW_{12}O_{40}$)⁵ and Wells-Dawson ($H_6P_2W_{18}O_{62}$) types⁶ of HPAs, but the effect of using DEAT as co-catalyst has not been explored just yet for the synthesis of DPA. HPAs hold great promise mainly due to their strong acidic character, although the exact acidity (pKa) cannot be given despite having been thoroughly studied¹⁵. They can be immobilized in various ways, i.e. on silica⁵, clay¹² or cesium¹¹ giving them excellent heterogeneous catalyst properties.

Scheme 3: Immobilization and activation of the difunctional precursor



In order to assess the potential of HPA-based systems, various compounds have been synthesized (Table 1), some of which already known to work for the synthesis of DPA (entries 4,5 and 6), others are only known to be active in the synthesis of BPA (entry 9), and finally some combining different positive improvements such as substituting W12 for W18 and the addition of DEAT(entries

7 and 10 respectively). W12 and amberlyst were used as homogeneous and heterogeneous reference respectively.

Entry		Conversion ^a	Yield ^b	Selectivity (pp')	Ref
1	HCl	65% LA		68.75	4,5,16
2	W12	60 % LA	30 % DPA	74%	6
3	Amberlyst	33.8 % LA	17% DPA	80 %	7,17
4	CsW12	28.3 % LA	27% DPA	80.4 %	4,5,16
5	CsW18	35.9 % LA	35% DPA	88%	6
6	SiO ₂ -W12	80 % LA	35% DPA	75%	4,5,16
7	SiO ₂ -W18	n.r. ^c	n.r. ^c	n.r. ^c	
8	CsW12	85% AC ^d	34%	40 % pp	14
9	CsDEATW12	95 % AC ^d	94%	96 % pp	14
10	CsDEATW18	n.r. ^c	n.r. ^c	n.r. ^c	

Table 1: Conversion, yield and selectivity (where available) for catalysts screened

^a %LA = levulinic acid conversion (for DPA synthesis), %AC= acetone conversion (for BPA synthesis)

^b No specification given on max possible yield

^c System not reported

^d System reported active for BPA synthesis

6.3 Experimental section

Levulinic acid, phenol, Tetraethyl orthosilicate (TEOS), 12-tungstophosphoric acid (H₃PW₁₂O₄₀), Cs₂CO₃ (99%), 2-diethylamino-ethanethiol hydrochloride, amberlyst, N-Methyl-N-(trimethylsilyl)trifluoroacetamide and P123 (MW 5800) were obtained from Sigma-Aldrich and used as received.

W18 was synthesized as described in¹⁸. SiO₂-W₁₂ and SiO₂-W₁₈ were synthesized according to the procedure described previously⁵. The heteropolyacid cesium salts CsW₁₂ and CsW₁₈ were prepared according to the method described in⁶, and successively functionalized with DEAT according to the procedure described in¹⁴

The condensation reaction was performed in a glass vessel sealed with a teflon cap and equipped with a magnetic stirrer at 100°C. The vessel was charged with phenol (1.28 g, 13.6 mmol) and Levulinic acid (0.395 g, 3.4 mmol), as well as 50

mg of catalyst. The mixture was stirred at a speed of 1200 rpm and the reaction time was set at 6, 8 or 24 hours and samples were taken during the reaction to track the conversion of the reagents.

6.3.1 Analysis

Samples were analyzed with a GC-MS (HP 6890 Series and HP 5972 Series, respectively). The column used was a Restek Rxi-5sil MS, with a length of 30.0 m, a diameter of 250 μm and a film thickness of 0.25 μm , using a split injector (ratio 50:1) and column flow of 0.8 ml/min and an injection temperature of 250°C.

The samples were prepared by adding 1 μl of reaction mixture to 1 ml THF with naphthalene (internal standard). To this mixture, between 20-30 μl of MSTFA (N-methyl-N-(trimethylsilyl)trifluoroacetamide) was added to silylate the products (phenol, levulinic acid and DPA) which was necessary in order to enable analysis by GC.

6.4 Results:

6.4.1 Elemental analysis of catalysts: calc. (found):

SiO₂-W12: Si: 37.33% (31.99%; 31.38%) P: 0.22% (0.0078%; 0.0155%)

SiO₂-W18: Si: 37.33% (35.06%; 34.24%) P: 0.28% (0.0638%; 0.1485%)

CS_{2.5}H_{0.5}PW₁₂O₄₀: Cs: 10.35% (9.54%; 10.12%)

CS_{1.5}H_{4.5}P₂W₁₈O₆₂: Cs: 4.37% (4.00%; 3.95%)

CS_{2.5}H_{0.25}DEAT_{0.25}PW₁₂O₄₀: N: 0.12% (0.12%; 0.13%) C: 0.56% (0.59%, 0.65%) H: 0.12% (0.18%, 0.16%) S: 0.25% (0.16%, 0.14%)

CS_{1.5}H_{2.25}DEAT_{2.25}P₂W₁₈O₆₂: N: 0.69% (1.18%; 1.26%) C: 3.33% (6.39%, 6.44%) H: 0.74% (1.49%, 1.46%) S: 1.48% (2.57%, 2.74%)

6.4.2 Activity:

The activity was determined from the conversion of levulinic acid and compared to the values reported previously (where applicable) (Figure 1). Unfortunately the method of analysis employed was not able to distinguish between both potential

isomers meaning no conclusions could be drawn about the selectivity of the catalysts.

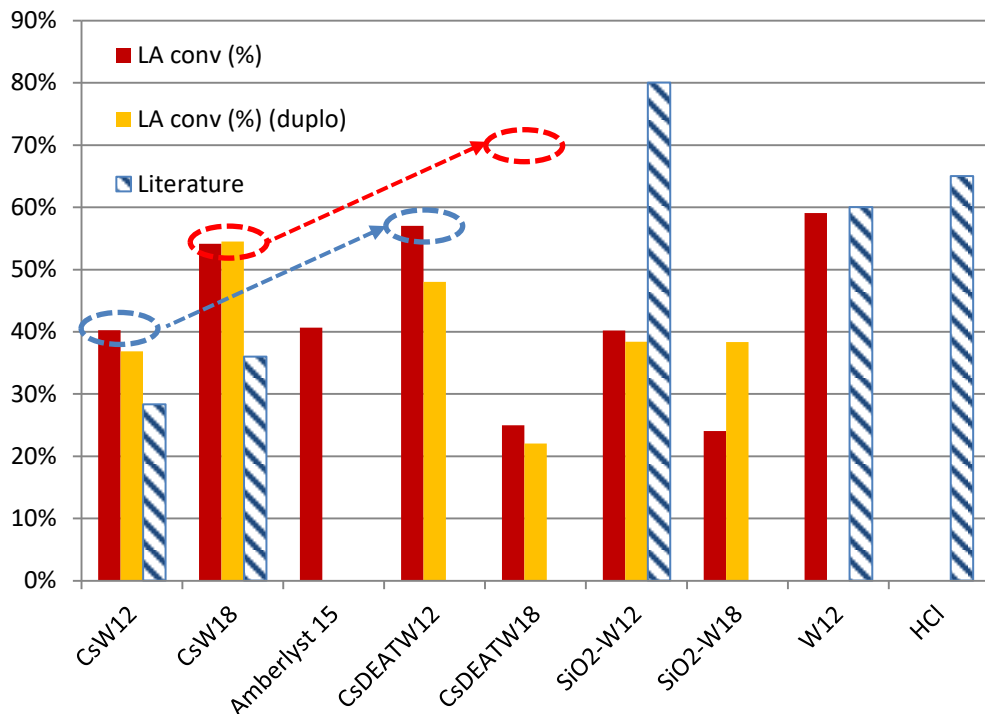


Figure 1: Activity towards the synthesis of DPA for the catalysts screened in this research

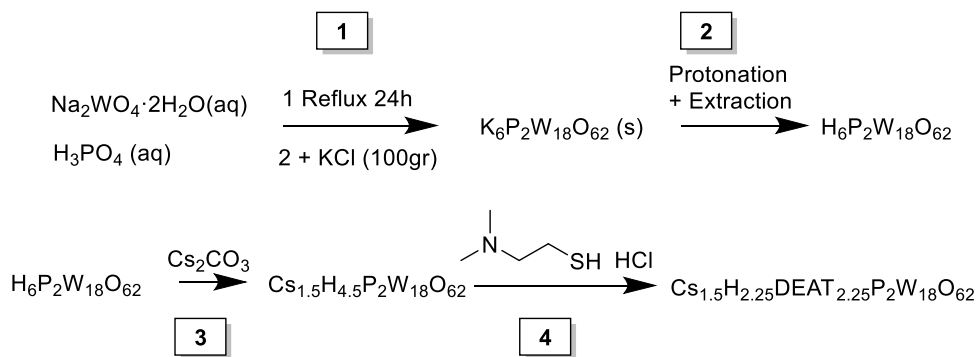
As expected the activity of amberlyst 15 is significantly lower than the homogeneous systems. Furthermore, the use of W12 as homogeneous catalyst unsurprisingly gives results very similar to that of hydrochloric acid¹⁶. Also nearly identical conversion compared to reported values⁶ have been obtained, indicating good reproducibility (dashed blue bars in Figure 1).

The same cannot be said about the silica-based systems, however: it proved difficult to reproduce the catalyst following the procedure described⁴. Elemental analysis showed that both the W12 and W18 variant showed virtually no presence of phosphorous, indicating failed immobilization of the HPA. This is reflected in the activities obtained.

Cesium immobilization of both W12 and W18 has been successful, giving excellent activities compared to reported values. The direct comparison with published activities is somewhat skewed however, as the selectivity of the system could not be determined. There is a notable effect discernable for the addition of DEAT to the CSW12 catalyst: an increase in conversion of roughly 15% was observed (blue dashed arrow in Figure 1) when comparing CsW12 and CsDEATW12. When looking at the CSW18 system this effect is not present however. (The expected increase in activity is depicted by the red dashed arrow)

The elemental analysis of CSDEATW18 showed a larger than expected amount of sulfur present in the material. This can be explained by taking a closer look at the synthetic procedure, depicted in Scheme 4. The first step consists of isolation of the intermediate as potassium salt (Scheme 4-1). This salt is then acidified and extracted as ether-adduct giving the desired W18 (Scheme 4-2). The next step consists of immobilization of the W18 on cesium carbonate by replacing part of the available protons (Scheme 4-3). Finally half of the available protons are replaced by DEAT (Scheme 4-4).

Scheme 4: Reaction scheme for the synthesis of CsDEATW18



Upon closer examination of the precursor via elemental analysis showed that the protonation step (Scheme 4-2) had been incomplete, yielding a material with a significantly reduced amount of available protons. (i.e. instead of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ the resulting material could probably be more accurately described as $\text{K}_2\text{H}_4\text{P}_2\text{W}_{18}\text{O}_{62}$). This error led to a final product which, rather than the desired 1:1 ratio of H:DEAT, contained a H:DEAT ratio of 0.06:1. Unfortunately, the procedure is rather complex, involving a multi-step synthesis, and while a likely culprit has been

identified in incomplete protonation, this is still an assumption. The results obtained by using CsDEATW12 are very promising however, and pave the way to further improvements. If a similar effect of the addition of DEAT is observed on the system based on W18, and the desired $\text{Cs}_{1.5}\text{H}_{2.25}\text{DEAT}_{2.25}\text{P}_2\text{W}_{18}\text{O}_{62}$ can successfully be synthesized, this would be a very promising candidate for a suitable and sustainable catalyst for the synthesis of diphenolic acid.

6.5 Part 2: Towards a real life application of a thermoreversible thermoset-like polymer: compounding with flax and jute fibers.

Upon application, many thermosetting resins are compounded with various additives such as pigments^{19,20}, flame retarding agents^{21,22} and/or filler materials. Fibrous fillers are very common as these can simultaneously reduce the weight and cost of the material while at the same time imparting desirable properties like improved (impact) strength to the material. For polyester resins the most commonly employed fibrous material is glass fiber. This trend is changing, however, as more and more initiatives are moving towards the use of sustainable fillers²³. Materials such as wood fibers²⁴, flax²², jute²⁵ and cellulose²⁶⁻²⁸ are being employed successfully. In order to evaluate the applicability of the thermoreversible polyester described in the previous chapters of this thesis compounds with fibrous materials have been prepared and tested. In order to preserve the sustainable nature of the material, the fibers used are all obtained from natural resources. Samples compounded with either flax or jute have been prepared containing 1%, 5% or 10% of the fibrous material (Figure 2). As the test bars were relatively small, the effect of inhomogeneity in the fibers has a significant effect on the outcome. It was therefore decided that in order to reduce this inhomogeneous nature the size of the fibers were reduced by freezing in liquid nitrogen, grinding using an industrial grinder and subsequently passed through a sieve tower. The fraction of 1-0.5 mm particle size was used in this experiment.

The polymer used for all samples was a furan functionalized polyester which was polymerized in the presence of a chain stopper (see chapter 3 of this thesis), the polymer (PE-fur) was used as a powder which was mixed with bismaleimide crosslinker in a ratio of maleimide to furan groups of 1:1. The fibers were mixed with the polyester and compounded in a hot press, both in T-bones and straight bars (Figure 3). Upon removing the samples from the mold the need for reinforcement became painfully clear as it proved challenging to remove the pure polyester samples intact: the high brittleness of the material ensured many cracks formed during this process. Nevertheless intact bars of all formulations were obtained. The fibers showed good dispersion throughout the material, and gave no signs of phase separation on the polymer/fiber interface.



Figure 2: Flax (left) and Jute (right) fibers used and fiber/polymer (PE-fur) mixtures (far right)

Unfortunately the brittleness of the polyester made measurements of its tensile strength impossible: the material would either slip from the clamps or crack due to the clamping force exerted upon it. This combined with a rather large experimental error gave rise to a very binary conclusion: the fact that tensile measurements could be successfully performed at all on samples containing fibrous reinforcements means that these are stronger than the unsupported base polymer. Any further quantification of this effect is unfortunately not possible from these results.

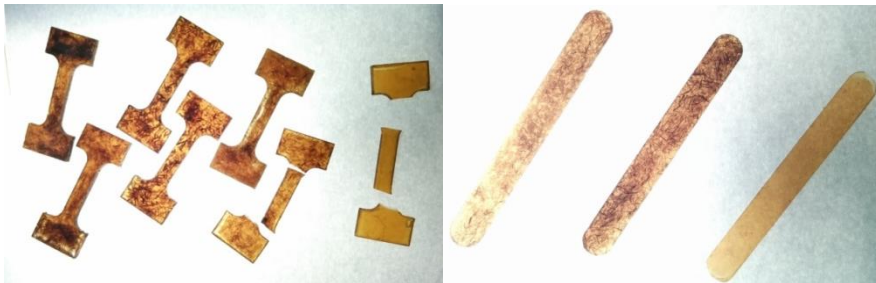


Figure 3: backlit photo of samples containing, left-to-right: 10%jute (2x), 10%flax (2x), 5%jute (2x), pure PE, 10%jute, 10%jute, 1%jute

In an attempt to obtain some quantifiable idea of the reinforcing properties of the polyester/fiber compound samples consisting of layered flax mats filled with polymer were compressed in a heated press. The resulting material showed excellent penetration of the polymer (Figure 4). There was little to no delamination of the layers, as observed by manual strumming of the sample.

Tensile testing of the compound as well as the fiber mats were performed, and once again no quantitative analysis could be performed as the cured samples could not be broken by the tensile machine, withstanding 5 kN of force. This proves only conceptually that the polyester can be reinforced easily and effectively by the addition of fibrous filler materials.

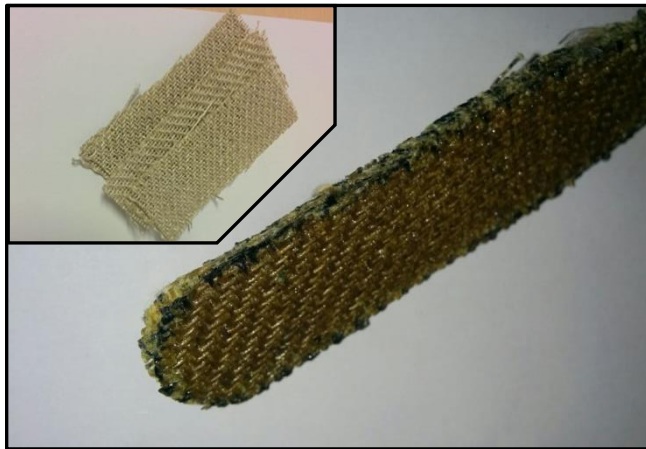


Figure 4: Flax fiber mat reinforced PE-fur composite, (inset) fiber mats used.

6.6 Conclusions

The possibility of compounding the polyester described in this thesis (PE-fur) with various renewable fibrous materials has been demonstrated by successfully obtaining samples containing various amounts of different fibers (i.e. flax and jute). This effectively yielded a nearly completely renewable composite, which is proven to be able to undergo thermoreversible crosslinking. Furthermore, when using flax mats good penetration of the polyester into the fiber mats was observed and the resulting material did not suffer from delamination, a common problem for layered composites²⁹. The exact (quantitative) effect of fiber reinforcements could not be established, unfortunately, as the virgin material could not be measured in the tensile testing machine.

6.7 Outlook

As stated in the conclusions of part 1, the synthesis of diphenolic acid from levulinic acid could greatly benefit from a heterogeneous catalyst. A very promising candidate would be the DEAT-functionalized, Cs-immobilized W18 heteropolyacid. Should the same increase in activity upon the addition of DEAT which was observed for the W12 system be obtained for the W18 system as well, a very potent system would be obtained.

Furthermore, as evident from part 2, the potential for property-enhancement through the application of fibrous filler materials is very high. The bio-based fillers tested display excellent compatibility with the base polymer and a significant increase in tensile strength, in fact when utilizing flax mats the tensile strength increase was so high that it was no longer possible to break the samples. This topic would benefit greatly from additional research. One area of interest could be the use of functionalized fillers where the fibrous materials are able to partake in Diels-Alder reactions with the polymer matrix.

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Summary

Thermoset materials are widely employed due to their superior chemical resistance and mechanical properties. The reason these materials perform so well is due to the fact that they consist of a three-dimensionally crosslinked network. One example of such a thermoset are unsaturated polyester resins which are able to form this network via the *in situ* polymerization of styrene. Unfortunately there are two main drawbacks tied to the use of these resins: styrene is a hazardous chemical which requires special precautions to work with. Furthermore the crosslinked network which gives the material its superior properties also ensures it is not recyclable in any way. Fortunately due to uncertainty in oil prices and availability and an increasing understanding of the effects of carbon emissions there is a global increase in awareness regarding the use of materials obtained from sustainable resources. In the polymer industry in particular large strides are being made to implement green alternatives for currently employed materials. While this might yield a less toxic alternative to styrene, this approach does nothing to address the problems that arise at product end of life, namely the waste generated upon disposal. The first chapter of this thesis gives an overview of some of the processes that have been successful in going green as well as various strategies to address the waste generated by enabling the recycling of the final material.

While the added functionality which is common in most biobased compounds often presents difficulties both in obtaining a pure compound as well as controlling any side reactions, they can sometimes present opportunities that were otherwise unavailable. An example of this is diphenolic acid, a diol obtained from the platform chemical levulinic acid which is a structural analogue to bisphenol A apart from an additional pendant acidic functionality. Realizing the potential of diphenolic acid, chapter 2 describes its modification along with the subsequent incorporation into a polyester. The modification consisted of the addition of a furan group, utilizing the acidic functionality present. Polymerization was performed with terephthaloyl chloride which gave an alternating polyester in good yields. As every other monomer in this polymer contained a pendant furane functionality the material could be easily crosslinked by the addition of

bismaleimide. The bismaleimide was able to react via the Diels-Alder reaction in order to create a three-dimensionally crosslinked material and due to the reversible nature of the Diels-alder reaction the material obtained could be decrosslinked by elevating the temperature. Unfortunately the temperature needed was too close to the degradation temperature resulting in loss of material properties.

The degradation of the polymer upon decrosslinking is tackled in chapter 3, which describes the optimization of reaction conditions during polymerization. As expected, the addition of phenol, which can act as a chain stopper during the polymerization reaction, results in short-chain polyesters. The reduction in chain length leads to a reduction in glass transition temperature of the uncrosslinked polymer, which in turn lowers the temperature of the decrosslinking reaction. As the processing and degradation temperature now lie further apart, the polymer no longer undergoes any degradation during processing. This is shown by successfully reworking spent polymer by grinding and remolding, resulting in samples with identical material properties as the original material.

Despite the excellent reworkability, the crosslinked polymer is very brittle, limiting its potential applications. Chapter 4 describes the efforts made to improve this by modifying the impact properties of the crosslinked polymer. In this chapter the preparation of various blends of the polyester with furan functionalized EPDM rubber is described. The furan functionality on both polymers enables covalent interactions via the Diels Alder reaction between both components in the polymer blend, reducing phase separation. A blanc experiment with a non-functionalized EPDM rubber was performed which showed no improvement on mechanical properties, whereas a correlation between rubber content and impact strength could clearly be seen for the furan functionalized EPDM. This is a strong indication for successful covalent interaction of the two components.

In order to further control the mechanical properties of the crosslinked polymer, compositions containing various bismaleimide crosslinkers in various amounts were prepared. The results of which are described in chapter 5. Upon analysis of the different compounds it became apparent that crosslinking was possible with a wide range of bismaleimide molecules. However for all formulations it was obvious that not each maleimide group participates in Diels-Alder coupling with a

furan in the final product. Even when half of the stoichiometric amount of bismaleimide relative to the furan groups present was added there was no visible effect on material properties.

Finally, chapter six briefly addresses the largest steps that need to be taken on the road to a truly sustainable product, namely the synthesis of the main precursor: diphenolic acid, as well as the implementation of the final polymer in fiber containing formulations. The synthesis of diphenolic acid could be greatly improved by the implementation of heterogeneous catalysts. Some preliminary experiments have shown that the use of immobilized heteropolyacids in combination with diethylaminothiol could be a good candidate for this reaction. Furthermore the compatibility of sustainable fiber materials (flax and jute) with the polymer matrix was tested. As the base polymer proved too brittle to be properly tested on a tensile machine only qualitative conclusions could be drawn from these compounds: the use of flax and jute improves the toughness of the resulting compound, also the use of jute mats yielded a compound which was able to withstand 5 kN of tensile force, a significant improvement.

Overall, the work in this thesis covers nearly the complete chain from platform chemical levulinic acid up until real life application in fiber reinforced materials. The successful recyclability and reworkability indicate that this polyester might be a sustainable alternative to the currently employed polyester resins.

Samenvatting

Thermoharder materialen worden veelal gebruikt vanwege hun uitstekende chemische resistentie en mechanische eigenschappen. De reden dat deze materialen zo goed presteren is vanwege het feit dat ze bestaan uit een driedimensionaal netwerk. Een voorbeeld van een dergelijk thermoharder zijn onverzadigde polyesterharsen welke in staat zijn dit netwerk te vormen door de *in situ* polymerisatie van styreen. Er zijn echter twee nadelen verbonden aan het gebruik van deze harsen: styreen is een toxische chemicalie waarvoor speciale voorzorgsmaatregelen nodig zijn om het te gebruiken. Verder zorgt het driedimensionale netwerk wat het materiaal zijn superieure eigenschappen geeft er tegelijk voor dat het op geen enkele wijze recycleerbaar is. Gelukkig is er door onzekerheid in olieprijzen en -beschikbaarheid en een groeiend begrip van de effecten van koolstofdioxide emissies een toename in het gebruik van materialen uit hernieuwbare bronnen. In de polymeerindustrie in het bijzonder worden grote stappen gezet om groene alternatieven voor de huidige materialen te introduceren. Hoewel dit zou kunnen resulteren in een minder toxisch alternatief voor styreen, doet deze aanpak niets om de problemen op te lossen die ontstaan aan het eind van de productlevensduur, namelijk het afval wat ontstaat na wegwerpen. Het eerste hoofdstuk van dit proefschrift geeft een overzicht van sommige van de processen die erin zijn geslaagd groene materialen te implementeren, alsook diverse strategieën om de afvalstroom aan te pakken door het mogelijk te maken de materialen te recycleren.

Hoewel de extra functionaliteit die voorkomt in de meeste groene chemicaliën meestal voor moeilijkheden zorgt, zowel in het verkrijgen van de pure uitgangsstof alsook het bedwingen van nevenreacties, kunnen ze soms ook unieke kansen bieden die anders niet mogelijk waren. Een voorbeeld hiervan is difenolzuur, een diol verkregen uit de platform-chemicalie levulinezuur wat een structurele analoge is van bisfenol A met als enig verschil een extra zuurgroep op een zijketen. Na het potentieel van difenolzuur te hebben ingezien wordt in hoofdstuk 2 de modificatie en vervolgens het inbouwen in een polyester beschreven. De modificatie bestaat uit het toevoegen van een furaan functionaliteit, gebruikmakend van de aanwezige zuurgroep. De polymerisatie

werd vervolgens uitgevoerd met tereftaloyl chloride wat resulteerde in een alternerende polyester in goede opbrengst. Aangezien elk tweede monomeer een furaan groep bevat kon het materiaal eenvoudig vernet worden door toevoeging van bismaleimide. Het bismaleimide was in staat te reageren via de Diels-Alder reactie zodat een driedimensionaal vernet product achterbleef. Vanwege het reversibele karakter van de Diels-Alder reactie kan het verkregen materiaal terug gaan naar de onvernette toestand door verhogen van de temperatuur. Helaas was de benodigde temperatuur te dicht bij de degradatietemperatuur wat resulteerde in een verlies van materiaaleigenschappen.

De degradatie van het polymeer tijdens dit ontkoppelen wordt aangepakt in hoofdstuk 3, wat de optimalisatie van reactiecondities beschrijft tijdens de polymerisatie reactie. Zoals verwacht resulteerde het toevoegen van fenol, wat dienst kan doen als ketenstopper tijdens de polymerisatie, in een korte-keten polyester. De verlaging van ketenlengte leidt tot een verlaging van de glasovergangstemperatuur van het pure polymeer, wat vervolgens de temperatuur van de ontkoppelingsreactie verlaagd. Doordat de degradatietemperatuur en de verwerkingstemperatuur verder uiteen liggen ondergaat het polymeer geen degradatie meer tijdens het verwerken. Dit is aangetoond door het succesvol hergebruiken van verbruikt polymeer door het te vermalen en opnieuw te vormen wat resulteert in nieuwe monsters met identieke materiele eigenschappen als het oorspronkelijke materiaal.

Ondanks dat het materiaal perfect herbruikbaar is, is het vernette polymeer zeer bros, wat de potentiële toepassingen beperkt. Hoofdstuk 4 beschrijft de gedane inspanningen om dit te verbeteren door de slagvastheid van het vernette polymeer te verbeteren. In dit hoofdstuk wordt de bereiding van diverse mengsels van het polyester en furaan gefunctionaliseerd EPDM rubber. De furaan functionaliteit aanwezig in beide polymeren maakt covalente interactie mogelijk door middel van de Diels-Alder reactie tussen de twee materialen in het polymeermengsel, wat voor een vermindering van het optreden van fasescheiding zorgt. In een blanco experiment waarin een niet furaan gefunctionaliseerd rubber werd toegevoegd was geen verbetering van mechanische eigenschappen zichtbaar, terwijl een correlatie tussen de hoeveelheid rubber en de slagvastheid duidelijk zichtbaar was voor het furaan gefunctionaliseerde rubber. Dit is een

sterke indicatie dat de beoogde covalente interactie tussen de twee componenten daadwerkelijk plaatsvindt.

Om de mechanische eigenschappen van het vernette polymeer verder te sturen zijn diverse formuleringen met verschillende soorten bismaleimide in verschillende verhoudingen. De resultaten zijn weergegeven in hoofdstuk 5. Na analyse van de verschillende materialen werd het duidelijk dat de vernettingsreactie mogelijk is met een breed scala aan verschillende bismaleimide moleculen. Voor alle formuleringen echter, was het duidelijk dat niet elke maleimidegroep deelneemt aan Diels-Alder koppeling met een furaangroep in het eindproduct. Zelfs wanneer slechts de helft van de hoeveelheid bismaleimide werd toegevoegd ten opzichte van de stochiometrisch benodigde hoeveelheid was er geen zichtbaar effect op de materiaaleigenschappen.

Tot slot komen in hoofdstuk 6 kort de grootste benodigde stappen aan bod die nog genomen dienen te worden op weg naar een volledig hernieuwbaar materiaal, namelijk de synthese van de voornaamste uitgangsstof: difenolzuur alsook de implementatie van het polymeer in vezel bevattende formuleringen. De synthese van dienolzuur kan erg verbeterd worden door het gebruik van een heterogene katalysator. Exploratieve experimenten hebben aangetoond dat het gebruik van een geïmmobiliseerd heteropolyzuur in combinatie met diethylaminothiol een goede kandidaat voor deze reactie kan zijn. Verder is de compatibiliteit van hernieuwbare vezelmateriaal (vlas en jute) met het polymeer getest. Aangezien het zuivere vernette polymeer te bros bleek om getest te worden op een trekbank konden er enkel kwalitatieve conclusies getrokken worden van deze formuleringen: het gebruik van vlas en jute verbeterd de sterkte van het materiaal. Ook is door het gebruik van jute matten een materiaal verkregen wat in staat was 5 kN trekkracht te weerstaan, ook een significante verbetering.

In zijn totaliteit beslaat het werk in dit proefschrift nagenoeg de hele keten van platform chemicalie levulinezuur tot een daadwerkelijk toepassing als vezel versterkte materialen. De succesvolle recycleerbaarheid en herbruikbaarheid zijn een sterke indicatie dat dit polyester een duurzaam alternatief kan zijn voor de huidige toegepaste polyesterharsen.

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List of publications

Thermally reversible rubber-toughened thermoset networks via Diels–Alder chemistry

R. Araya-Hermosilla, G. Fortunato, A. Pucci, P. Raffa, L. Polgar, A.A. Broekhuis, P. Pourhossein, G.M.R. Lima, M. Beljaars, F. Picchioni
European Polymer Journal, Volume 74, January 2016, Pages 229–240

Bio-based aromatic polyesters reversibly crosslinked via Diels-Alder reaction

M.Beljaars, H.J.Heeres, L.Mevius, A.A.Broekhuis, F.Picchioni
Submitted to European Polymer Journal

The effect of molecular weight on the (re)-processability and material properties of bio-based, thermoreversibly cross-linked polyesters

M.Beljaars, H.J.Heeres, A.Kamphuis, A.A.Broekhuis, F.Picchioni
Submitted to Polymer

Enhancing the impact properties of two Diels-Alder functionalized polymers through blending

M.Beljaars, H.J.Heeres, G.Fortunato, L.M.Polgar, R.Araya-Hermosilla, A.A.Broekhuis, F.Picchioni
Submitted to Journal of Applied Polymer Science

The influence of amount and type of crosslinker on thermal and mechanical properties of a thermoreversibly crosslinked biobased polyester.

M.Beljaars, H.J.Heeres, A.A.Broekhuis, F.Picchioni
In preparation

Conference proceedings

Oral contributions:

BIO-based Composite RESins M. Beljaars, L.Mevius, M.Molla, A.Kamphuis, E.Gandini, F.Picchioni, H.J.Heeres, A.A.Broekhuis, First annual ENTEG meeting , Haren, the Netherlands, 2015

Public choice award for best presentation

Jury award for best presentation

Bio-based and renewable polymeric materials, M. Beljaars, L.Mevius, M.Molla, A.Kamphuis, F.Picchioni, H.J.Heeres, A.A.Broekhuis, third international Conference on Recycling and reuse of materials (ICRM-2014), Kottayam (Dist) Kerala, India 2014

Bio-based composite resins, M. Beljaars, L.Mevius, M.Molla, A.Kamphuis, F.Picchioni, H.J.Heeres, A.A.Broekhuis, R. Blaauw (WUR), J. van Haveren (WUR), Biobased Performance Materials symposium 2013, Wageningen, the Netherlands, 2013

Bio-Based Composite Resins, M.Beljaars, POLYMAR 2013 IST International Conference in Polymers with special Focus in Early Stage Researchers, Barcelona, Spain 2013

Poster contributions:

Novel polymer based on levulinic acid capable of reversible crosslinking “going green” is not enough, M.Beljaars, L.Mevius, A.A.Broekhuis, H.J.Heeres, F.Picchioni, Biobased Performance Materials symposium 2012, Wageningen, the Netherlands

“Going green” is not enough RuG contribution to BIOCREs, M.Beljaars, L.Mevius, A.A.Broekhuis, F.Picchioni, Biobased Performance Materials symposium 2013, Wageningen, the Netherlands

Novel biobased recyclable polymers “going green”is not enough, M.Beljaars, A.A.Broekhuis, H.J.Heeres, F.Picchioni, Biobased Performance Materials symposium 2014, Wageningen, the Netherlands

Novel biobased recyclable polymers “going green”is not enough, M.Beljaars, A.A.Broekhuis, H.J.Heeres, F.Picchioni, 9th International Materials Technology Conference and Exhibition (IMTCE 2014), Kuala-Lumpur, Malaysia 2014
Second poster prize

Novel biobased recyclable polymers “going green”is not enough, M.Beljaars, A.A.Broekhuis, H.J.Heeres, F.Picchioni, NPS14, Utrecht, the Netherlands, 2014